$H_2B_4O_7$
$H_3BO_3$
$H_2Cr_2O_7$
$HClO_3$
$H_2Cr_2O_4$
$HMnO_4$
$HClO$
$H_2MnO_4$
$H_2IO_3$
$Pb + HNO_3 = Pb(NO_3)_2 + NO + H_2O$
$PbCrO_4$
$Cd + HNO_3 = Cd(NO_3)_2 + NO + H_2O$
$SnCl_4$
$Ag + HNO_3 = AgNO_3 + NO + H_2O$
$Cu(NO_3)_2$
$(NH_4)_2SO_4$
$Na_2SnO_2$
$(NH_4)_3AsS_4$
$Ag_3AsO_4$

A COURSE IN

# INORGANIC CHEMISTRY

## FOR COLLEGES

BY

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D. C. HEATH & CO., PUBLISHERS

BOSTON NEW YORK CHICAGO

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# PREFACE

THIS book is intended for college students who devote a year to general chemistry. It is primarily a students' book, and is not designed to replace the large text-books, which are better suited for reference than for class use. The descriptive portions of the text include the well-established topics usually taught in a year of college chemistry, though considerable space is devoted to the application of modern principles to chemical industries. The theoretical portions include not only the principles whose value was demonstrated long ago, but also many recent conceptions, which are fast becoming indispensable in interpreting chemical and physical phenomena. Some of the theoretical topics, which are distributed through the text at serviceable points, are the theory of electrolytic dissociation, reversible reactions, equilibrium, catalysis, vapor pressure, electrolysis, and the behavior of dissolved substances. It is hoped that the book as a whole will be found adequate for all students whose work is confined to a year and will likewise serve as a broad foundation for those who continue the study of chemistry.

In the preparation of the manuscript and correction of the proof, judicious advice was received from Professor Frank W. Durkee, Tufts College, Tufts College, Mass., Assistant Professor William Foster, Princeton College, Princeton, N.J., Professor Arthur J. Hopkins, Amherst College, Amherst, Mass., Professor James F. Norris, Simmons College, Boston, Mass., Professor Charlotte F. Roberts, Wellesley College,

Wellesley, Mass., Professor Benjamin W. Van Riper, Wheaton College, Wheaton, Ill., and others. The author is grateful to these teachers for their help, but he assumes entire responsibility for all statements in the book.

L. C. N.

Boston University, Boston, Mass.,
January, 1909.

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# A COURSE IN
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# INORGANIC CHEMISTRY

## CHAPTER I

### Physical and Chemical Changes — Matter — Energy — Elements — Compounds

CHEMISTRY is one of the natural sciences. By a natural science we mean an organized group of knowledge devoted primarily to the study of matter and energy. There are several of these groups. Some, like geology, deal for the most part with the concrete aspects of science, while others, like chemistry and physics, are concerned with both abstract and concrete phases. The different groups of natural sciences are not independent. Indeed, they often overlap and have indefinite boundaries. This has always been characteristic of chemistry and physics, and recent study has drawn them even more closely together.

The scope of chemistry is rather difficult to outline, especially at the outset of its study. Hence it is only possible at this stage to present a preliminary and somewhat incomplete conception, leaving to future pages its development, interpretation, and application. Chemistry deals with the properties of matter; with the changes involved in the transformations of different kinds of matter, with numerous laws, theories, and hypotheses summarizing chemical phenomena, and with the manufacture and utilization of a vast number of substances indispensable to mankind.

**Properties of Matter.** — Different substances are recognized and distinguished by their properties. Thus, some

substances are solid, others liquid, and still others gaseous, though the special physical state of a substance depends usually upon its temperature. For example, water, mercury, and many other substances, which are liquid at the ordinary temperature, become solid if cooled to a low temperature and gaseous if heated to a high temperature. Other familiar properties are color, odor, taste, relative weight, crystalline structure, luster, hardness, melting point, boiling point, and solubility. Many properties are exhibited when substances are subjected to the action of light, electricity, and particularly to a wide range of temperature. But the most important properties are doubtless those exhibited when different substances act upon each other and thereby produce the profound changes characteristic of chemistry.

Let us consider some properties of the substance sulphur. Observation shows it is a solid which has a yellow color, no odor, no taste, and a crystalline structure. It is relatively heavier than water, because it sinks when placed in a vessel of water, but it is insoluble in water. Experiment shows that when sulphur is heated, it melts into a pale yellow liquid, which turns brown at a comparatively low temperature and remains so until the temperature is quite high, whereupon it becomes viscous like tar and finally boils, yielding a yellow smoke which looks much like sulphur. In the light sulphur has luster, *i.e.* it reflects light. It does not conduct electricity, for when introduced into the circuit of an ordinary electric bell, it prevents the electricity from ringing the bell; on the other hand, when rubbed with a cloth, sulphur becomes electrified and attracts tiny pieces of paper. If a piece of sulphur is heated to a high temperature, it takes fire and burns. The flame is blue, and an invisible, suffocating product is detected by the odor; if burned long enough, all the sulphur is transformed into this gas. Finally, if sulphur and a powdered metal, such as iron or copper, are

mixed and heated in a test tube, the mixture begins to glow, the incandescence often spreading throughout the mass even after the test tube has been removed from the flame. The product is neither sulphur nor iron but a black substance having properties quite different from those of the original constituents. Thus, step by step, we have established by observation and experiment those properties which serve to identify sulphur and to distinguish it from all other substances. By a similar though often more elaborate and complicated procedure the properties of all substances can be discovered, recorded, and classified.

**Changes in Matter and Classification of Properties.** — Observation and experiment show that substances often change or can be changed. These changes are shown by a change in properties. Sometimes the change merely involves a temporary change in properties. Thus, water can be changed into steam or ice, and iron can be magnetized or melted, but the water and iron are not thereby fundamentally altered. Apparently they are changed into new substances, but they are not essentially changed, for, although some of the properties are new, rigid examination shows that no new substances have been formed. The steam, ice, magnetized iron, and melted iron are still the substances chemically known as water and iron. Indeed, it is only necessary to cool the steam and the melted iron and to melt the ice to obtain the original substances, which are familiar as water and iron. [Changes which do not involve the transformation of substances into new substances are **physical changes.**] In physical changes the change in a substance is often only temporary and is due to some change in or departure from the conditions which usually prevail, *e.g.* a change in temperature, pressure, or electrical conditions, and as soon as these new conditions are removed the substance regains its

familiar properties. Thus, when iodine is heated in a test tube, the solid iodine turns into a beautiful violet vapor which solidifies in the colder part of the test tube, where it may be recognized as iodine by its steel-gray color and crystalline form. The iodine has not been transformed into a new substance, but is merely changed physically, assuming for the time being properties characteristic of iodine at a higher temperature than the ordinary.

Very often, however, substances are changed fundamentally, their essential nature is affected, and the change is manifested by the formation of new substances. The original substance with its properties disappears, often completely, and one or more new substances with characteristic properties appear. Thus, coal is readily changed into ash and an invisible gas which have properties totally unlike those of coal. The change is permanent, too, for the ash and gas are new substances and do not become coal again as soon as they are cold. Changes which involve the transformation of substances into new substances are **chemical changes.**

An examination of the properties of sulphur recorded above reveals two classes which are more or less distinct. Color, odor, taste, relative weight, crystalline structure, luster, and electrical behavior are exhibited by unchanged or unchanging sulphur. They are associated with physical changes, and their manifestation does not involve a disappearance of the substance nor its transformation into another substance. Thus, sulphur is readily recognized as sulphur during its immersion in water or its electrification by rubbing. Properties exhibited during physical changes or by an unchanging substance are called **physical properties.** On the other hand, certain properties — not always readily detected — are exhibited only by chemical changes. Their manifestation involves a fundamental change in the nature

of substances. Thus, sulphur burns in air and unites chemically with iron, thereby forming new substances; oxygen, as we shall see later, readily undergoes chemical transformation, uniting with many substances; furthermore, many substances are decomposed into other substances by heat or electricity. Those properties — not essentially physical — manifested by substances when they undergo chemical changes are called **chemical properties.**

It is clear from the foregoing paragraphs that typical physical changes are characterized by the alteration of physical properties, while chemical changes are characterized by the formation of one or more new substances. Examples of familiar physical changes are changes in physical state (illustrated by the formation of ice and vapor from water, and *vice versa*), production of the colors in the sky, magnetization of iron, and electrification of glass. Familiar chemical changes are the rusting of iron, burning of oil in a lamp, digestion of food, souring of milk, and combustion of wood.

It is not always possible to separate physical and chemical properties into two sharply defined classes nor to call certain changes entirely physical or exclusively chemical. Some chemists advocate the adoption of a third class of changes, viz. **physico-chemical changes,** such as fusion (*i.e.* melting) and solution. Thus, when sulphur is boiled or dissolved in some liquid, properties are exhibited which are in part physical and in part chemical. For example, if boiled sulphur is poured while still hot and thick into water, the product is a brown, plastic, gummy mass totally unlike the original sulphur in appearance though it reverts to ordinary, yellow sulphur in time; similarly, powdered sulphur disappears (*i.e.* dissolves) in the liquid carbon disulphide, and is apparently converted into another substance, though it can be readily recovered, often as beautiful yellow crystals, by evap-

orating the liquid. Many substances besides sulphur when fused (*i.e.* melted) or dissolved exhibit properties which do not readily fall into either of the classes mentioned above. Such properties are often called **physico-chemical properties**.

**Chemical Action.** — When emphasis is laid upon the chemical change, the participating substances or **reagents** are said to undergo **chemical action**, to interact, or to react. This mutual or reciprocal action is called a **chemical reaction**. Usage of these terms is not uniform, but they are used in this book in the sense just stated. Thus, when copper is put into dilute nitric acid, the evidence of physical change in the acid is the rise in temperature, but this is quite subordinate to the evidence of chemical change, viz. the gradual disappearance of the copper, the liberation of a brown gas, and the production of a new substance which dissolves readily in the acid and colors it blue. Further experiment confirms these observations, for when some of the blue acid solution is evaporated, a blue solid is left which dissolves in water, gives off the brown gas when heated, and also forms a solution which deposits copper upon an iron nail. Chemical action has clearly taken place and the whole phenomenon was a chemical reaction.

Reactions are often complicated, but extensive study has shown that there are four general kinds, — combination, decomposition, substitution, and double decomposition. These will be illustrated and discussed in appropriate places.

**Matter and Energy.** — All changes studied in chemistry involve matter and energy.

It is sufficiently accurate for our present purpose to define **matter** as substance revealed to our senses by properties, the fundamental property being weight. In chemical changes matter is transformed; that is, substances are so changed that new substances are formed. Such changes, as we have

already learned, involve a substitution of new properties for old ones. One property of substances, however, is not changed, viz. the weight. Careful and extensive study shows that the total weight of the substances participating in a chemical change is apparently unaltered. This means that the sum of the weights of the substances which enter into a chemical change equals the sum of the weights of the new substances resulting from the chemical change. This feature of chemical change is sometimes briefly summed up by saying, "matter is indestructible." This rather comprehensive statement is one form of a law called the **Law of the Conservation of Matter.** It is preferably stated thus: —

*No weight is lost or gained in a chemical change.*

Observation shows that work is done by motion, heat, light, and electricity. Thus, at Niagara Falls the water turns wheels which are connected with dynamos, and the electricity generated thereby is used to operate street cars, furnish light, and produce the heat which is used in certain chemical industries. The term **energy** is applied to whatever produces work or can be converted into work. For example, motion, heat, light, and electricity are familiar forms of energy, and are usually studied in physics. In chemistry we study these forms and also another form, called chemical energy. Energy, like matter, is transformable, yet apparently constant in amount. Observation of the actual transformations of the different forms of energy is an everyday experience. Coal in burning gives up its chemical energy in the form of heat, and the heat becomes motion. In an electric battery chemical energy is changed into electricity, which in turn becomes motion in a bell, or heat in a cooking utensil, or light in a metal wire, or even chemical energy in an electroplating apparatus. All chemical changes involve a transformation of energy. The chemical energy is locked up, so to speak, in substances, and when

chemical changes occur there is a transformation and redistribution of energy. Thus, the heat which is often needed to start chemical changes really becomes transformed, in part at least, into chemical energy, while the heat produced by chemical changes is the result of the transformation of some of the chemical energy into heat. So also the light which is essential in photography is transformed into chemical energy and locked up as such in the chemicals on the photographic plate. Food contains chemical energy, and when food is digesting, this energy is being transformed into heat, which maintains the temperature of the body. But all these transformations involve no loss or gain in the total amount of energy involved. When a known amount of heat is put into a substance and stored up as chemical energy, as it were, that heat can be recovered as heat or as an equivalent amount of some other form of energy. The amount of chemical energy is always altered in chemical changes, but the total amount of energy involved is unchanged. The characteristics of energy are often summarized in a brief statement called the **Law of the Conservation of Energy**, thus : —

*Energy can be transformed without loss, but cannot be (by any known means) created or destroyed.*

**Chemical Elements and Chemical Compounds.** — In chemistry we study almost exclusively two classes of substances, viz. elements and compounds. Mixtures, especially the kind of mixture known as a solution, receive some attention. Chemical compounds consist of chemical elements united with one another. There are thousands of compounds, but only about eighty elements.

**Chemical Elements.** — An extensive examination of many different kinds of matter has shown that certain kinds can be decomposed at will into two or more substances totally

unlike the original matter, but that other kinds are not reducible by any means at present under our control. Water, for example, can be decomposed into the gases, hydrogen and oxygen, which are entirely different from water. But neither hydrogen or oxygen can be decomposed by any known process. Furthermore, oxygen and hydrogen cannot be transformed into each other by any known process. Other substances can be added chemically to oxygen or hydrogen, but nothing can be taken away from them chemically nor produced from them chemically without an increase in weight. That is, when oxygen or hydrogen undergoes chemical change, there is addition, an increase in weight, a transformation into a new substance having new properties, and especially a greater weight than the original amount of oxygen or hydrogen; these chemical changes are never accompanied by loss in weight. Furthermore, oxygen and hydrogen have characteristic properties; some are much alike, while others are totally different. Oxygen and hydrogen are elements, and all other kinds of matter which have fundamental characteristics typified by oxygen and hydrogen are likewise elements. The essential properties of the chemical elements will be set forth as we proceed with our study of the elements and their compounds. It has been customary for many years to regard elements as those substances which cannot be decomposed into simpler substances or transformed without loss of weight. It would follow from this traditional definition that the elements are the primary forms of matter, so to speak, and are chiefly characterized by stability. This is true of most elements, as far as we know. But our inability to decompose elements does not necessarily mean that they are immutable under all conditions. Indeed, their instability is shown by the spontaneous decomposition of certain elements, especially radium. Nevertheless, it is sufficient for our present purpose to regard the chemical elements as

the fundamental materials from which compounds are formed and to which compounds are finally reduced. Questions concerning transmutation can be postponed until more facts are available.

Each element is designated by a symbol, which is an abbreviation of its name. The following is an alphabetical

TABLE OF IMPORTANT ELEMENTS AND THEIR SYMBOLS

| NAME | SYMBOL | NAME | SYMBOL |
|---|---|---|---|
| Aluminium | Al | Lead | Pb |
| Antimony | Sb | Lithium | Li |
| Arsenic | As | Magnesium | Mg |
| Barium | Ba | Manganese | Mn |
| Bismuth | Bi | Mercury | Hg |
| Boron | B | Nickel | Ni |
| Bromine | Br | Nitrogen | N |
| Cadmium | Cd | Oxygen | O |
| Calcium | Ca | Phosphorus | P |
| Carbon | C | Platinum | Pt |
| Chlorine | Cl | Potassium | K |
| Chromium | Cr | Silicon | Si |
| Cobalt | Co | Silver | Ag |
| Copper | Cu | Sodium | Na |
| Fluorine | F | Strontium | Sr |
| Gold | Au | Sulphur | S |
| Hydrogen | H | Tin | Sn |
| Iodine | I | Zinc | Zn |
| Iron | Fe | | |

The elements are not uniformly distributed in nature, either in abundance or mode of occurrence. Our knowledge of the relative abundance of the elements is based on a study of the atmosphere, the ocean, and a shell of the earth's crust about ten miles deep. The approximate distribution of matter in these three portions of the globe is seen in the following

TABLE OF THE DISTRIBUTION OF MATTER

| | |
|---|---|
| Atmosphere | .03 per cent |
| Ocean | 7.08 per cent |
| Shell of Earth's Crust | 92.89 per cent |

The atmosphere contains about 20 per cent of oxygen, 79 per cent of nitrogen, and 1 per cent of argon. The distribution of the elements in the ocean appears in the following

TABLE OF THE APPROXIMATE COMPOSITION OF THE OCEAN

| ELEMENT | PER CENT | ELEMENT | PER CENT |
|---|---|---|---|
| Oxygen | 85.79 | Sulphur | .09 |
| Hydrogen | 10.67 | Calcium | .05 |
| Chlorine | 2.07 | Bromine | .008 |
| Sodium | 1.14 | Carbon | .002 |
| Magnesium | .14 | Other Elements | traces |

Besides the elements which are combined as saline matter, the ocean contains dissolved gases, such as oxygen, nitrogen, and carbon dioxide.

The proportion of the elements in the ten-mile shell of the earth's crust is shown in the following

TABLE OF THE APPROXIMATE COMPOSITION OF THE EARTH'S CRUST

| ELEMENT | PER CENT | GRAPHIC PROPORTION |
|---|---|---|
| Oxygen | 47.07 | |
| Silicon | 28.06 | |
| Aluminium | 7.90 | |
| Iron | 4.43 | |
| Calcium | 3.44 | |
| Potassium | 2.45 | |
| Sodium | 2.43 | |
| Magnesium | 2.40 | |
| Remainder | 1.82 | |

These elements are chiefly in the combined state.

It appears from the tables above that only ten elements are abundant. The globe as we know it is chiefly made up of a very few elements, which in both their free and combined states provide most of the substances studied in chemistry.

Many of the familiar metals are elements; *e.g.* lead, zinc, aluminium, tin, copper, iron, gold, and silver. Other elements besides the metals are solids, such as sulphur, carbon, and phosphorus; two are liquid, viz. bromine and mercury; while several are the common gases, oxygen, nitrogen, and hydrogen.

The following is a

TABLE OF THE LESS COMMON ELEMENTS AND THEIR SYMBOLS

| NAME | SYMBOL | NAME | SYMBOL |
|---|---|---|---|
| Argon | A | Radium | Ra |
| Beryllium | Be | Rhodium | Rh |
| Cæsium | Cs | Rubidium | Rb |
| Cerium | Ce | Ruthenium | Ru |
| Columbium | Cb | Samarium | Sm |
| Erbium | Er | Scandium | Sc |
| Europium | Eu | Selenium | Se |
| Gadolinium | Gd | Tantalum | Ta |
| Gallium | Ga | Tellurium | Te |
| Germanium | Ge | Terbium | Tb |
| Helium | He | Thallium | Tl |
| Indium | In | Thorium | Th |
| Iridium | Ir | Thulium | Tm |
| Krypton | Kr | Titanium | Ti |
| Lanthanum | La | Tungsten | W |
| Molybdenum | Mo | Uranium | U |
| Neodymium | Nd | Vanadium | V |
| Neon | Ne | Xenon | Xe |
| Osmium | Os | Ytterbium | Yb |
| Palladium | Pd | Yttrium | Yt |
| Praseodymium | Pr | Zirconium | Zr |

The **symbols** of the chemical elements, as may be seen in the foregoing tables, are in some instances the first letter of the common name of the element. Thus, O is the symbol of oxygen, H of hydrogen, N of nitrogen. But since several elements have the same initial letter, the symbol of some elements contains two letters. Thus, C represents carbon, while the symbol of calcium is Ca, of chlorine Cl, of chromium Cr, and of copper Cu. The symbols of several elements, especially the metals so long known, are derived from their Latin names. Thus, we have a

TABLE OF THE CHEMICAL ELEMENTS WITH LATIN SYMBOLS

| ELEMENT | LATIN NAME | SYMBOL | ELEMENT | LATIN NAME | SYMBOL |
|---|---|---|---|---|---|
| Antimony . | Stibium | Sb | Mercury . | Hydrargyrum | Hg |
| Copper . . | Cuprum | Cu | Potassium . | Kalium | K |
| Gold . . . | Aurum | Au | Silver . . | Argentum | Ag |
| Iron . . . | Ferrum | Fe | Sodium . . | Natrium | Na |
| Lead . . . | Plumbum | Pb | Tin . . . | Stannum | Sn |

The symbols of the elements always begin with a capital letter, and are not followed by a period. They should be learned by actual use. Their full significance will be explained in later chapters.

**Chemical Compounds.** — When elements unite with each other or participate in a chemical change, the result is the formation of one or more chemical compounds. The elements which make up a chemical compound are called its constituents. Chemical compounds differ fundamentally from elements and have two essential characteristics. (1) Their constituents are not mixed, but are united chemically. That is, the chemical energy originally possessed by the elements that make up compounds has so operated that

the new substance (*i.e.* the compound) cannot be separated into its constituents except by the application of some form of energy, such as heat, light, electricity, etc. Thus, water is a compound of the elements oxygen and hydrogen, which cannot be separated from each other unless water is subjected to intense heat or to electricity. (2) In any given chemical compound the constituents are always the same and are present in a fixed ratio by weight. Thus, pure table salt, however prepared or wherever found, always contains 39.34 per cent of sodium and 60.65 per cent of chlorine.

The foregoing characteristics, together with others, specially those exhibited when certain compounds and elements undergo chemical change, will be fully discussed in succeeding chapters.

Chemical compounds must not be confused with mixtures. The components of a mixture may vary in nature and in proportion; they are also not combined chemically but held together loosely, and can be separated by some mechanical operation, as filtering or sifting, without bringing about any chemical change by the application of energy. A mixture, too, generally has properties which are similar to, or are an average of, those of its components.

### Problems

1. Solve the problems on the metric system in the Appendix, § 1.

## CHAPTER II

### Oxygen — Ozone

OXYGEN has played an important part in the development of chemistry, and is an appropriate element with which to begin a systematic study of this science.

**Occurrence.** — Oxygen is the most abundant and widely distributed of the elements, and occurs both free and combined. Mixed with nitrogen and a few other gases, it forms nearly 21 per cent (by volume) of the atmosphere. Combined with hydrogen, it constitutes eight ninths (by weight) of water; combined with silicon and certain metals, it makes up nearly half of the earth's crust; while compounds of oxygen with carbon and hydrogen form a large part of animal and vegetable matter. Starch, for example, which is a component of all plants, contains about 50 per cent oxygen.

**Preparation.** — Oxygen can be obtained from its compounds or from air. It was first prepared by decomposing a compound of oxygen and mercury called mercuric oxide. When heated, this compound decomposes into oxygen and mercury; the oxygen escapes as a gas, and the mercury condenses as globules or a film on the upper part of the glass vessel in which the experiment may be conveniently performed. This experiment is historically interesting, because it was first performed by Priestley, the discoverer of oxygen. (See Discovery of Oxygen, below.)

The gas is often prepared by decomposing potassium chlor*ate* — a compound of oxygen, chlorine, and potassium. If heated to a rather high temperature, the potassium chlorate passes through a series of changes which result finally in the liberation of all the oxygen and the formation of a compound of potassium and chlorine called potassium chlor*ide*.

Oxygen is most conveniently prepared in the laboratory by heating a mixture of potassium chlorate and manganese

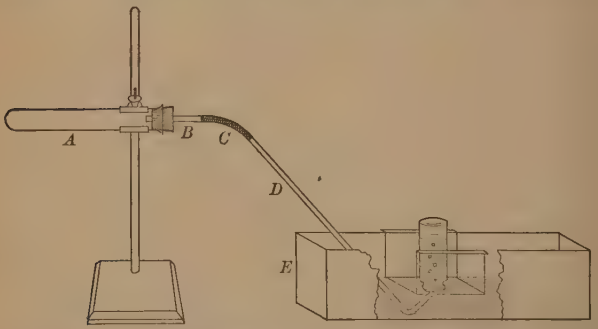


FIG. 1. — Apparatus for preparing and collecting oxygen in the laboratory. The oxygen mixture is put in *A* and heated. The oxygen gas escapes through *B*-*C*-*D* into the pneumatic trough (*E*). The latter is filled with water until the shelf is covered and a bottle full of water is then placed mouth downward on the shelf. The oxygen bubbles through the hole in the shelf up into the bottle and displaces the water.

dioxide in a glass or metal vessel, and collecting the liberated oxygen in a bottle by means of a pneumatic trough. (See Fig. 1.) The gas is liberated freely from this mixture at a lower temperature than when either compound is heated alone. Large quantities of oxygen are prepared for commercial purposes by heating a mixture of potassium chlorate and manganese dioxide in an iron vessel.

Other commercial processes are used. In Brin's process, which is operated largely in England, purified air is forced by a pump over barium oxide heated to about 700 degrees C.,[1] thereby forming barium dioxide. The air supply is then cut off, and the pressure in the retorts reduced by reversing the pump. This operation changes the barium dioxide back again into barium oxide and oxygen. The gas is drawn off into a reservoir. The process is then repeated. A kilogram of barium oxide yields about ten liters of oxygen at a single operation.[2]

Oxygen can also be separated from liquid air. (See Liquid Air.) By allowing liquid air to evaporate at ordinary temperature and pressure, the nitrogen escapes from the liquid air more rapidly than the oxygen, leaving finally a liquid which is nearly pure oxygen. Unlimited quantities of oxygen may probably thus be cheaply prepared from the air.

Oxygen can be prepared from oxone (the commercial name of a compound of oxygen and sodium) by allowing it to interact with water. This is a convenient method for preparing a small quantity of the gas.

**Chemical Changes illustrated by the Preparation of Oxygen.** — Brief reference has already been made to the four main kinds of chemical change, viz. decomposition, combination, substitution, and double decomposition. The first and second kinds are illustrated by some of the methods for the preparation of oxygen. When mercuric oxide is heated,

[1] C. is the abbreviation of "centigrade," which is the name of the thermometer used in science. This thermometer registers 100 degrees at the boiling point of water, and 0 degrees at the freezing point. (See Appendix, § 2.)

[2] "Kilogram" and "liter" are denominations of the metric system of weights and measures. This system should be learned or reviewed. (See Appendix, § 1.)

it decomposes into oxygen and mercury. Energy in the form of heat serves to start and maintain the chemical change, and if heat were supplied long enough, all the compound would be decomposed into the two elements oxygen and mercury. A chemical change whereby a compound with a definite set of properties decomposes into two elements each with its own set of properties is the simplest illustration of the kind of chemical change called **decomposition**. This fact might be compactly expressed by an equation, thus: —

Mercuric Oxide = Mercury + Oxygen.

This equation also emphasizes the fact that the sum of the weights of the mercury and oxygen equals the weight of the mercuric oxide decomposed — a fact readily proved by weighing the three substances. When potassium chlorate is heated until all the oxygen is liberated, the chemical change is also a decomposition. In this case, however, the products are the element oxygen and the compound of potassium and chlorine called potassium chloride. The heat is not sufficient to produce the complete decomposition of potassium chlorate into its three elementary constituents. That is, decomposition stops when all the oxygen has been liberated. These facts might be expressed thus : —

Potassium Chlorate = Potassium Chloride + Oxygen.

**Decomposition** in general, then, is a chemical change whereby a compound is separated chemically into two or more new substances. The preparation of oxygen from barium oxide and the oxygen of the air illustrates both combination and decomposition. In the first stage, when barium oxide is heated in a current of air, the compound, barium oxide, unites chemically with the element, oxygen, and thereby produces a new compound (barium dioxide). A chemical change whereby two or more elements or compounds unite

to form a new compound is called **combination.** The second stage in the preparation of oxygen by the method under discussion is another illustration of decomposition. Thus, barium dioxide decomposes into barium oxide and oxygen. The two chemical changes might be expressed thus : —

(1) Barium Oxide + Oxygen = Barium Dioxide.
(2) Barium Dioxide = Barium Oxide + Oxygen.

The equations used in this paragraph to summarize the facts connected with decomposition and combination are crude forms of the chemical equation. Subsequently it will be shown that a definite relation exists between the weights of the substances used and produced and that this relation can be expressed accurately in the form of an equation. At the present stage the rather cumbersome equation used above is convenient because it emphasizes two facts about chemical change; viz. (1) chemical change involves no change in the total weight of the substances, and (2) chemical change results in the formation of new substances.

**Properties.** — Pure oxygen gas has no color, odor, or taste. It is somewhat soluble in water, one hundred liters of water dissolving about three liters of oxygen under ordinary conditions. The presence of even a small proportion of dissolved oxygen is exceedingly important. Fish die in water containing no dissolved oxygen; and the oxygen absorbed by flowing water helps keep it free from organic matter. (See Decay, below.) Oxygen is slightly heavier than air, its density being 1.105 on the air standard. This means that under the same conditions of temperature and pressure a given volume of oxygen is 1.105 times heavier than an equal volume of air. One liter of oxygen weighs 1.429 grams at a temperature of 0° C. and under a barometric pressure of 760 millimeters. Subsequently it will be shown that the volume

of a gas depends upon the temperature and the pressure, the normal or standard temperature and pressure being respectively 0° on the centigrade (C.) thermometer and 760 millimeters (mm.) on the barometer. Oxygen like other gases has three physical states. Liquid oxygen is pale blue. It boils at $-182.5$ °C. under the normal pressure of the atmosphere; at this temperature its specific gravity is 1.13 (*i.e.* it weighs 1.13 times an equal volume of water). It is magnetic, for when a strong electromagnet is held near it, the liquid is attracted by the magnet just as iron filings are by an ordinary magnet. Solid oxygen has a whitish color. The properties of oxygen enumerated in this paragraph are physical properties, because their exhibition does not involve a transformation of the oxygen into a new substance.

The most striking chemical property of oxygen is the ease with which it combines or interacts with other substances. It belongs to the class of active chemical elements, and the chemical changes it undergoes are attended by varied and interesting physical changes. Oxygen forms compounds with all the other single elements except fluorine, bromine, argon, and helium (and the other inert gases in the atmosphere). With most of them the union is direct; *i.e.* the two elements unite chemically to form a compound having oxygen and the other element as constituents. This direct combination is often accompanied by light and heat, though the temperature at which combination occurs varies between wide limits. At the ordinary temperature oxygen unites slowly with most elements, though with phosphorus the chemical action is quite rapid, as may be seen by the glow and fumes when the end of a sulphur match is rubbed, especially in the dark. Metals, such as lead, zinc, and copper, tarnish or rust slowly; *i.e.* they combine slowly with the oxygen of the air. The chemical activity of oxygen at high temperatures is readily shown by putting burning or

glowing substances into it. All burn vividly in oxygen. It interacts chemically with the substances, and the intensity of the chemical energy is shown by the heat and light evolved.

The vigorous chemical activity of oxygen can be shown by simple experiments. When a glowing stick of wood is put into oxygen, the wood instantly bursts into flame; and if left in the oxygen, the wood continues to burn brightly until the gas is exhausted. If faintly glowing charcoal is put into oxygen, the charcoal glows vividly. Sulphur burns in air with a feeble, blue flame, but in oxygen the flame is much larger and brighter. The flame in both cases is accompanied by a gaseous product which smells like a burning sulphur match. Iron wire does not burn in air, but if the end is coated with burning sulphur and then put into a bottle of oxygen, the wire burns vividly, throwing off a shower of sparks; a globule of white-hot molten iron oxide is often seen on the end of the wire, and sometimes the inside of the bottle is coated with a reddish powder, which is mainly a compound of iron and oxygen. Iron and oxygen combine at a higher temperature than do sulphur and oxygen, so the heat from the burning sulphur is needed to start the chemical action between the oxygen and the iron. When lighted magnesium is put into oxygen, the burning metal instantly becomes surrounded with a dazzling flame, and burns rapidly to a white powder, thus showing that the temperature at which it begins to combine with oxygen is much lower than that in the case of iron.

**Test for Oxygen.** — The conspicuous behavior of a glowing stick or burning substance when put into oxygen enables us to distinguish oxygen from all other gases except one (see Nitrous Oxide). Thus, if a glowing stick is thrust successively in three bottles of gas and relights in one, that gas is probably oxygen. This critical examination to establish

the identity of oxygen is called testing or making a test. Each element has properties which respond to appropriate tests. All compounds likewise behave in some decisive way when subjected to tests. These tests have been established by extensive investigation and are extremely useful in chemistry.

**Chemical Changes illustrated by the Chemical Properties of Oxygen.** — In all the chemical changes described in the preceding paragraphs two features are conspicuous, viz. the loss of physical properties of the interacting elements and the formation of new substances. The carbon (of the wood and charcoal), iron, sulphur, and magnesium are no longer recognizable as such in the compounds produced by the chemical change. The oxygen likewise disappears; for although two products are gases, their properties are not those of oxygen. Thus, one gas (carbon dioxide) extinguishes flames and the other (sulphur dioxide) has a suffocating odor. The chemical change in the case of the four elements just mentioned is **combination**. The oxygen was added chemically to each element and the product was a compound of the two elements called an oxide. Their names are carbon dioxide, sulphur dioxide, ferrous-ferric oxide, and magnesium oxide. Any compound whose constituents are oxygen and one other element is an **oxide.** (See Oxides, below.) The chemical change in the case of wood is not simple combination. Wood contains chiefly a compound of carbon, hydrogen, and oxygen, which is first decomposed by heat, and then the carbon and the hydrogen combine individually with oxygen as in the other cases.

**Oxidation.** — When sulphur, iron, magnesium, and carbon (in wood and charcoal), and other elements burn in oxygen, they combine rapidly with it. This change is **oxidation.**

Oxidation almost invariably produces heat, though in slow oxidation the heat is not readily detected and is sometimes overlooked. Very rapid oxidation is accompanied by light.

The fact that **burning** in its simplest aspect is a combining with oxygen can be easily verified. It has been repeatedly shown that oxygen is one constituent of all the products formed by burning substances in that gas. Thus, carbon forms an invisible gas called carbon dioxide, which is a compound of carbon and oxygen. Similarly, sulphur, iron, and magnesium form compounds of these elements and oxygen. These facts may be further verified by a simple experiment. If mercury is heated, it gains in weight, and red particles collect on its surface; but if it is protected from the air by some coating and then heated, there is no gain in weight and no evidence of the red product. Therefore, when the exposed mercury is heated, something from the air must be added to it. Now, if the red substance is collected and heated in a glass tube, mercury and oxygen are the only products. Hence, the exposed mercury, when heated, must have combined with the oxygen of the air.

The process of oxidation is not always so simple as that described in the preceding paragraph. Often one or more of the constituents of a compound is seized upon by the oxygen, so to speak, and converted into an oxide. Hydrogen is especially liable to be thus removed from such compounds as contain it. Hence oxidation, which is primarily a combining with oxygen, is often a complex process resulting in the decomposition of a compound and the formation of one or more oxides.

Oxidation is not always rapid enough to produce light and appreciable heat. Thus, iron and other metals rust and wood decays slowly, but both processes are essentially oxidation. Sometimes slow oxidation develops considerable heat. Thus, oily rags, piles of hay, and heaps of coal often

take fire unexpectedly, because the heat produced by the continued oxidation cannot escape. Fires caused by such oxidation are sometimes said to be due to spontaneous combustion.

Many substances give up oxygen readily and are called **oxidizing agents**. In this class belong potassium chlorate, which is used in fireworks, and potassium nitrate, which is an ingredient of gunpowder. In the process of oxidation, oxidizing agents lose oxygen, and are said to undergo reduction; the latter process will be more fully described in the next chapter.

**Oxides** have already been defined as compounds of oxygen and one other element. There are many oxides, and their names often express in a general way their composition. Oxides of different elements are distinguished by placing the name of the element (or a slight modification of it) before the word *oxide*, *e.g.* magnesium oxide, lead oxide, zinc oxide, nitric oxide, ferric oxide. Sometimes *di-*, or a similar numerical syllable, is prefixed to the word *oxide*, *e.g.* carbon monoxide, manganese dioxide, barium dioxide, sulphur trioxide, phosphorus pentoxide. The significance of the prefix is explained later.

**Combustion.** — In ordinary language combustion means fire or burning. Substances which kindle and burn readily are called combustible, while those which burn with difficulty or not at all are called incombustible. In a limited sense, **combustion** is rapid oxidation accompanied by heat and often also by light. Oxygen is essential to ordinary combustion. If air is excluded from a fire, the fire goes out. When wood, coal, paper, oil, or any other combustible substance burns, the carbon (of which they partly consist) unites with the oxygen of the air, thereby forming the invisible gas carbon dioxide, while the chemical change is attended by

heat and light. Briefly, a burning substance is uniting rapidly with oxygen. But since air is only about one fifth oxygen (the remainder being chiefly nitrogen, which does not support combustion), combustion is less rapid and hence less vigorous in air than in oxygen. The compounds formed during combustion are oxides; in the case of fuel they are usually carbon dioxide and water — the latter being hydrogen oxide. The temperature at which combustion takes place varies between wide limits. Some substances, like phosphorus and gasolene vapor, catch fire at a moderate temperature, while others do not burn until heated to the very highest temperatures. Each substance has its own **kindling temperature**, *i.e.* the temperature to which it must be heated before it will catch fire, though this temperature depends somewhat on the form of the substance as well as upon its nature. Application of this fact is seen in the use of paper and kindling wood in starting a fire in a stove.

The correct explanation of fire, burning, and combustion was first made by Lavoisier (1743–1794). For many years chemists had believed that all combustible substances contained a principle called *phlogiston*, and that when a substance burned, phlogiston escaped. Very combustible substances were thought to contain much phlogiston, and incombustible substances no phlogiston. This theory of combustion was proposed by Becher (1635–1682) and advanced by Stahl (1660–1734). Many famous chemists — Priestley, Scheele, and Cavendish — supported it. Lavoisier, in 1775, proved by his own and others' experiments that phlogiston did not exist, and that ordinary combustion is a process of combination with "a certain substance contained in the air." Soon after he identified this substance as oxygen.

Combustion, in a broad sense, is not exclusively oxidation, but any chemical change which is attended by light and heat. Thus, hydrogen and other elements burn in chlorine, and phosphorus often produces heat and light by its combinations with other elements than oxygen. This broader meaning will be illustrated and discussed later.

**Relation of Oxygen to Life.** — Oxygen is essential to all forms of animal and plant life. If an animal or a plant is deprived of air, it dies. By respiration air is drawn into the lungs, where part of its oxygen is given to the blood; this oxygen, which is distributed to all parts of the body by the blood, oxidizes the tissues of the body. By this slow oxidation waste products are formed and heat is supplied to the body. One of these waste products is carbon dioxide gas, which with other gases is exhaled from the lungs. New tissue is built up from the food we eat. The human body resembles a steam engine. In each, the oxygen of the air helps burn fuel largely composed of carbon. In the engine, the products escape through a chimney and the heat produced is used to form steam which moves parts of the machine; in the body, the products escape mainly through the lungs and the heat keeps the body at the temperature at which it can best perform its functions.

The vital necessity to fish of the small proportion of oxygen dissolved by water should be recalled in this connection.

It was formerly believed that breathing pure oxygen would produce too rapid oxidation in the body and burn up the tissue faster than it could be made. But recent study shows that with proper precautions oxygen may be breathed by a healthy person without producing any harmful effect. The blood apparently absorbs a maximum quantity of oxygen, whether supplied from the air or from the pure gas. Oxygen is often administered to a person who has been suffocated, or to one who is unable to inhale enough air, as in cases of croup, asthma, or extreme weakness. It is sometimes used to sustain life when air is impure, as in mines or in diving bells and submarine boats, and during balloon ascensions to a great height.

**Decay** is in part oxidation. The oxygen of the air together with water vapor acts upon animal and vegetable matter

and slowly oxidizes it or burns it up. The decomposition is often begun and hastened by bacteria. The oxygen dissolved by water assists in the decay of impurities constantly flowing into rivers. So also it oxidizes injurious organic matter in the air. Hence, running water, because more perfectly exposed to the air, is more likely to be purer than standing or stagnant water, and the air in the open country or at the seashore purer than in the crowded city. The gaseous products of decaying matter are usually harmless. For all these reasons oxygen is an efficient purifying agent.

**Uses of Oxygen.** — Oxygen for commercial use is stored under pressure in strong iron cylinders. The pure gas has limited use, since air, although it contains about 80 per cent of the inert gas nitrogen, can usually be used in the place of oxygen. A mixture of oxygen and hydrogen burned in a suitable apparatus produces an intensely hot flame, which is sometimes used to melt refractory metals and to produce the calcium light. (See Oxyhydrogen Blowpipe.)

**Discovery of Oxygen.** — Oxygen was discovered on August 1, 1774, by Priestley (1733–1804). He prepared it by focusing the sun's rays upon red mercuric oxide by means of "a burning lens of twelve inches focal distance." It was independently discovered by Scheele (1742–1786), a Swedish chemist, about the same time.

Priestley called the gas dephlogisticated air because he regarded it as "devoid of phlogiston." Scheele called it empyreal air, *i.e.* fire air or fire-supporting air, because it assisted combustion. Lavoisier, in 1778, gave it the name oxygen (from the Greek *oxus*, acid, and *gen*, the root of a verb meaning to produce) because he believed from his experiments that oxygen was necessary for the production of acids — a view now known to be incorrect.

### Problems

1. Potassium chlorate contains about 39 per cent of oxygen. How many grams of oxygen can be prepared from 725 gm. of potassium chlorate?

2. What approximate weight of oxygen can be prepared from 100 gm. of potassium chlorate containing 12 per cent of impurity?

3. What is the weight of (*a*) 10 l. of oxygen. (*b*) 75 l., (*c*) 500 cc., (*d*) 750 cc., (*e*) 4 l. (at standard temperature and pressure)?

4. A room 25 m. long, 17 m. wide, and 15 m. high is filled with oxygen. What weight of gas does it contain?

5. Perform the problems in the Appendix, § 2.

## Ozone

**Ozone** is a gas related to oxygen, though its properties differ.

**Formation and Preparation.** — Ozone is formed when electric sparks pass through the air, and is therefore produced when electrical machines are in operation and during thunder storms. Slow oxidation, especially of moist phosphorus, produces ozone. Its formation accompanies the burning of hydrogen (in oxygen), and the passage of electricity through a solution of sulphuric acid and water. Ozone is prepared by subjecting pure, dry oxygen to a silent electric discharge.

**Properties.** — Ozone has a peculiar odor, suggesting burning sulphur. The name *ozone* signifies smell. It has a bluish color, and at a low temperature condenses to a blue liquid. Liquid ozone boils at $-119°$ C. under atmospheric pressure. It is an active oxidizing agent, tarnishing metals, bleaching colored vegetable substances, deodorizing foul animal matter, and corroding such substances as cork and rubber. When heated to 250° C., or higher, it is wholly changed into oxygen. When oxygen is changed into ozone,

it is found that three volumes of oxygen yield two volumes of ozone; and, conversely, the two volumes of ozone, when heated, become three volumes of oxygen. Hence, volume for volume, ozone is 1.5 times heavier than oxygen. Its theoretical relation to oxygen will be subsequently discussed.

**Uses.** — Pure ozone is seldom prepared, but air containing ozone is used to sterilize drinking water, and to a limited extent in bleaching oils and purifying starch.

## CHAPTER III

### Hydrogen

**Occurrence.**—Free hydrogen gas is present in the gases which escape from volcanoes, petroleum wells, and natural gas openings. Artificial illuminating gas contains considerable hydrogen. It is a product of fermentation and decay, and according to recent observations a very small quantity is present in the atmosphere of the earth. Enormous quantities of free hydrogen exist in the atmosphere of the sun, and during an eclipse of the sun gigantic streams of glowing hydrogen may be seen shooting out from the sun's disk thousands of miles into space. Other heavenly bodies contain hydrogen. Meteorites, which come from regions far beyond our earth, sometimes contain free hydrogen.

Combined hydrogen is abundant and widely distributed. It forms about one ninth (by weight) of water. Animal and vegetable substances contain hydrogen in combination with oxygen and carbon, and sometimes nitrogen. It is an essential constituent of all acids. Combined with carbon, it forms many gases and liquids called hydrocarbons, which are constituents of illuminating gas, kerosene, and gasolene. Combined with carbon and oxygen, it forms such compounds as sugar, starch, paper, wood, and numerous artificial products. With nitrogen it forms the familiar compound, ammonia, and with sulphur, the bad smelling gas, hydrogen sulphide, which occurs in many sulphur springs.

**Preparation.** — Hydrogen, like oxygen, is prepared from its compounds. This is accomplished by allowing certain

metals and acids to interact. The metals usually employed are zinc, iron, or magnesium, and the acids are dilute sulphuric acid or hydrochloric acid. The hydrogen comes from the acid and bubbles through the liquid, when the acid and metal are mixed. Hydrogen is prepared in the laboratory by putting the metal and dilute acid in a glass vessel provided with a delivery tube arranged to collect gas over water in a pneumatic trough. No flame should be near during the performance of this experiment, because a mixture of air and hydrogen explodes violently when ignited. The interaction of zinc and sulphuric acid produces, besides hydrogen, a compound called zinc sulphate. This remains in solution in the generator, and if that residual liquid is evaporated, the zinc sulphate separates from the solution as transparent crystals, which soon turn white in the air.

Hydrogen can be obtained from water by allowing sodium or potassium to react with it. If a small piece of sodium is dropped upon cold water, the sodium melts into a shining globule, which spins about rapidly on the surface with a hissing sound, and finally disappears after a slight explosion. But when the sodium is wrapped in a piece of tea lead pierced with a few holes and then dropped beneath the shelf of a pneumatic trough filled with water, the action proceeds smoothly; hydrogen gas rises and displaces the water from a test tube or bottle supported over the hole in the shelf.

Hydrogen can also be prepared by the interaction of steam — the gaseous form of water — and certain other metals, if they are heated. This experiment was first performed by Lavoisier, in 1783, while he was studying the composition of water. He passed steam through a red-hot gun barrel containing bits of iron, and hydrogen escaped from the tube. Since Lavoisier was studying the composition of water and not the properties of hydrogen, he naturally thought of this gas as essential for forming water. So he says in his notes,

"No name appears to us more suitable than that of hydrogen, that is to say, 'generative principle of water.'" Apart from historical interest, this experiment has commercial importance, for if steam is passed over white-hot coal (instead of iron), producer gas is formed. This mixture consists of about one-half hydrogen, and is used as a source of heat in making steel and glass. If oil vapor is added to this mixture, water gas is formed. This is an illuminating gas, and is used in many cities. (See Water Gas.)

Hydrogen, together with oxygen, is liberated from water by passing a current of electricity through water containing a little sulphuric acid. (See Chapter V.)

**Chemical Changes illustrated by the Preparation of Hydrogen.** — The preparation of hydrogen by the interaction of a metal and an acid illustrates the third kind of chemical change, viz. substitution, or, as it is sometimes called, displacement or replacement. Zinc and dilute sulphuric acid are usually used. The hydrogen is displaced from the acid and the zinc takes its place; *i.e.* zinc is substituted chemically for hydrogen. The chemical change is not essentially different from decomposition and combination, for we might picture the acid as decomposing into two fundamental parts, one part escaping as hydrogen gas, the other part (the sulphur and oxygen) at once combining with the zinc to form the new compound, zinc sulphate. It is better, however, to regard **substitution** as a chemical change in which one element replaces another in a compound, thereby producing a different element and a different compound. The chemical change in the preparation of hydrogen from zinc and sulphuric acid can be expressed by the following equation: —

$$\text{Zinc} + \text{Sulphuric Acid} = \text{Hydrogen} + \text{Zinc Sulphate}.$$

The preparation of hydrogen by the interaction of water and sodium is also a case of substitution. Here the sodium dis-

places one half of the hydrogen of the water, thereby producing free hydrogen and a new compound (sodium hydroxide), which consists of sodium, oxygen, and the rest of the hydrogen. The sodium hydroxide dissolves in the water in the trough. Briefly, sodium is substituted for hydrogen. The change can be expressed thus: —

Sodium + Water = Hydrogen + Sodium Hydroxide.

**Physical Properties.** — Hydrogen has no taste or color. The pure gas has no odor, though hydrogen as ordinarily prepared may have a disagreeable odor, due to impurities. Hydrogen is the lightest known substance. One liter of dry hydrogen at 0° C. and 760 mm. weighs only 0.08987 gm. Volume for volume, hydrogen is about 14.4 times lighter than air and about 16 times lighter than oxygen.

Fig. 2. — Pouring hydrogen upward.

The extreme lightness of hydrogen can be easily shown. (1) If a wide-mouth bottle of the gas is left uncovered two or three minutes and a lighted match then dropped in, the match will continue to burn. If hydrogen had been present, it would have combined with the oxygen of the air with a loud explosion, as soon as the flame of the match reached the mixture. (2) If a bottle of hydrogen is held beneath a bottle of air in the position shown in Figure 2, the gases exchange places, the hydrogen, owing to its lightness, rising into the upper bottle. Its presence there can be readily shown by inserting a lighted match into this bottle; if the experiment has been properly done, the hydrogen will burn quickly and quietly, but in most cases a loud explosion shows that only a part of the hydrogen has succeeded in entering the upper bottle. A lighted match dropped into the other bottle reveals air, or a mixture of air and hydrogen (if the experiment

has been performed too hastily). (3) If a small collodion, or rubber, balloon is filled with hydrogen and then released, it will rise rapidly into the air. Hydrogen, because of its lightness, is used to fill balloons; but ordinary illuminating gas, which is cheaper, is sometimes used.

Hydrogen is not very soluble in water, but it is absorbed by several metals, especially the rare metal palladium. The absorption of gases by metals is called **occlusion**. Only about 1.84 l. of hydrogen at 760 mm. pressure dissolve in 100 l. of water at 20° C. Palladium absorbs from 300 to 900 times its own volume of hydrogen, according to the conditions of the experiment. Platinum, gold, and iron act similarly, though to a less degree. Illuminating gas, which contains considerable hydrogen, is also absorbed by certain metals. Heat is developed by occlusion. This heat may be sufficient to raise the metal to a red heat and to ignite the gas itself. One form of self-lighting gas burner acts on this principle. Occlusion is partly chemical and partly physical.

Hydrogen diffuses readily; *i.e.* it quickly passes through porous substances, mixes with other gases without stirring or agitating, and freely escapes into space in all directions. Hydrogen has the highest rate of diffusion, because its density is the lowest, it being a general fact that the rate of diffusion of a gas is inversely proportional to the square root of the density. Thus, the rate of diffusion of hydrogen is four times that of oxygen, since the density of oxygen is sixteen times that of hydrogen. We are largely indebted for our knowledge of diffusion to the English chemist, Thomas Graham (1805–1869).

Liquid hydrogen is colorless and transparent. It was first obtained by Dewar in 1898. At the ordinary pressure of the atmosphere liquid hydrogen boils at $-252.5°$ C. When cooled to about $-256°$ C. by evaporation under reduced pressure, the liquid becomes a mass of solid hydrogen; the latter

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is a white froth if produced while boiling, and a transparent, ice-like solid if cooled when quiet. Solid hydrogen melts at — 260° C. (if the pressure is 58 mm.).

Hydrogen is not poisonous, if pure. It does not support life, but a little may be breathed without danger. When the lungs are filled with it, the voice becomes very thin and shrill.

**Chemical Properties.** — Hydrogen combines readily with several elements, especially chlorine, oxygen, sulphur, and nitrogen. The conditions favorable for combination vary greatly.

When organic matter containing nitrogen and sulphur decays, the products include ammonia and hydrogen sulphide. The former is a compound of nitrogen and hydrogen, and the latter of sulphur and hydrogen. Hydrogen and chlorine gases do not unite in the dark, but in the sunlight they combine with explosive violence even at the ordinary temperature. Hydrogen gas burns quietly in chlorine gas. The flame is bluish white, not very hot, and the product is hydrochloric acid gas — a compound of hydrogen and chlorine. This burning of hydrogen and chlorine illustrates the broader use of the word *combustion.* No oxygen is involved. It is a chemical change attended by light and heat and belongs to the class of changes called combination, since the hydrogen and chlorine are added or combined chemically.

Hydrogen and oxygen do not unite at the ordinary temperature, but at about 650° C. the gases combine with explosive violence. This temperature is provided by an ordinary flame or red-hot wire. A mixture of hydrogen and air explodes when ignited. Therefore, the air should be fully expelled from the apparatus in which hydrogen is being generated before the gas is collected, and no flame, large or small, should be near. Neglect of these precautions

has caused serious accidents. A small jet of hydrogen, however, burns quietly in air or oxygen. The flame is almost invisible and very hot. Water is the sole product of the combustion of hydrogen. The equation for this chemical change is: —

$$\text{Hydrogen} + \text{Oxygen} = \text{Water}.$$

These properties of the hydrogen flame can be readily shown by generating hydrogen in a suitable apparatus and lighting the dry gas as it issues from a small opening (Fig. 3). A platinum wire quickly becomes red hot in the

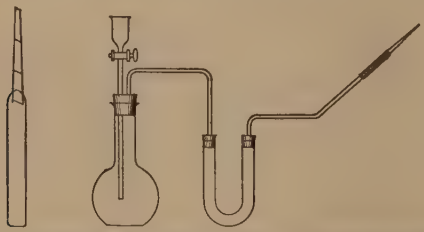


FIG. 3. — Apparatus for burning hydrogen. Acid is slowly introduced through the funnel into the flask, which contains zinc. The liberated hydrogen is dried as it passes through the U-tube containing calcium chloride and is lighted at the platinum tip after all the air has been driven from the apparatus. The tip, which is attached to the delivery tube by a small rubber tube, is shown (about actual size) on the left.

flame, and a dry inverted bottle into which the flame is inserted becomes coated on the inside with moisture condensed from the steam. The film of water often noticed on the bottom of a vessel placed over a lighted gas range or a Bunsen burner is formed by the burning of the hydrogen and of the hydrogen compounds in the illuminating gas. The fact that water is the only product of burning hydrogen was first shown in 1783 by Cavendish (1730–1810).

Lavoisier in the same year verified this fact and utilized it to explain the composition of water.

The temperature of the hydrogen flame is very high. More heat is produced by burning hydrogen and oxygen than by burning the same weight of any other substance.

Hydrogen does not support combustion, as the term is usually used. This property is illustrated by putting a lighted taper into an inverted bottle of hydrogen. The taper ignites the hydrogen, which burns at the mouth of the bottle, but the taper does not burn inside the bottle. Hence, hydrogen burns, but does not support combustion. When the extinguished taper is slowly withdrawn through the burning hydrogen, however, it is relighted, owing to the intense heat of the burning hydrogen.

**Test for Hydrogen.** — The test for hydrogen is that it extinguishes a flaming stick but is lighted at the same time, often with an explosion, and continues to burn until the gas is exhausted.

**The Oxyhydrogen Blowpipe** utilizes the intense heat produced by burning a mixture of hydrogen and oxygen. The apparatus (Fig. 4) consists of two pointed metal tubes. The inner and smaller one is for the oxygen, and the outer and larger one for the hydrogen. Their pointed ends are close together, and the two gases mix as they are forced out of these small openings by the pressure maintained in the storage tanks. Sometimes the tubes are separated, but the gases flow from a similar opening. The hydrogen is first turned on and lighted at the pointed opening, then the oxygen is turned on and the flow gradually regulated until the flame is the desired size, usually thin, straight,

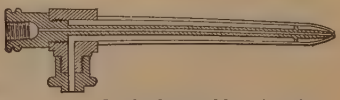


Fig. 4. — Oxyhydrogen blowpipe tip.

and as long as required. There is no danger in using the blowpipe, provided it does not leak and the pressure of the gases is properly regulated by the stopcocks. In the hot flame, some metals, like silver, turn to vapor; some, like iron, burn brilliantly; while others, like platinum, melt. When the flame strikes against a piece of lime, the latter becomes intensely bright. Thus used, it is called the lime, calcium, or Drummond light, and is often employed in operating the stereopticon.

The blast lamp is a modification of the oxyhydrogen blowpipe. The apparatus (Fig. 5) consists of two tubes, an inner one for air and an outer one for illuminating gas. The air, which is forced through the apparatus by a bellows, provides oxygen, while the illuminating gas contains hydrogen and other combustible gases. The mixture burns at the opening of the tubes with a colorless or bluish flame, which is hotter than the Bunsen flame (the usual source of heat for chemical experiments). The shape and size of the flame are easily regulated by stopcocks. The blast lamp is used as a source of heat for many operations in the laboratory, especially in chemical analysis.

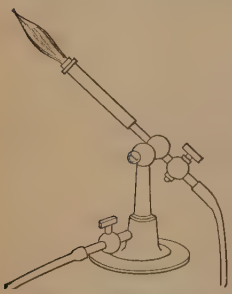


Fig. 5. — Blast lamp.

**Reduction.** — Hydrogen not only combines energetically with free oxygen, but it also withdraws oxygen from compounds. The chemical removal of oxygen is called **reduction.** Hydrogen is a vigorous reducing agent, just as oxygen is an energetic oxidizing agent. When oxides of certain metals are heated in a current of hydrogen, the oxygen of the oxide is removed and combines with the hydrogen

to form water; the metal is left uncombined. Thus, by heating lead oxide in hydrogen, water and metallic lead are produced. Chemically speaking, the lead oxide is reduced by the hydrogen. The chemical change is substitution (the hydrogen being substituted chemically for the metal), and it can be expressed thus : —

Hydrogen + Lead Oxide = Water + Lead.

This chemical change can also be interpreted from the standpoint of oxidation, because the hydrogen is oxidized to water at the same time the lead oxide is reduced. In fact, the processes of reduction and oxidation are closely related and usually occur in the same chemical change; either one may be emphasized in interpreting the change. It is preferable, however, at this stage to define reduction as the removal of oxygen from a compound, postponing the details of the process until more facts are available. In its simplest form, reduction is the opposite of oxidation.

**Discovery of Hydrogen.** — Paracelsus in the sixteenth century obtained hydrogen by the interaction of acids and metals. It was identified as an element in 1766 by Cavendish, who called it inflammable air. The name *hydrogen*, given to it by Lavoisier, in 1783, is derived from the Greek word *hudor*, water, and *gen*, the root of a verb meaning to produce. (See Preparation of Hydrogen, third paragraph.)

### Problems

1. What volume does 2 gm. of hydrogen occupy (at 0° C. and 760 mm.)?

2. The density of chlorine is nearly thirty-six times that of hydrogen. Compare its rate of diffusion with that of hydrogen.

3. A certain gas passes through a porous partition 2.5 times slower than hydrogen. What is its density?

4. How many times heavier than a liter of hydrogen is a liter of oxygen, both being dry and under standard conditions?

5. What is the weight of (*a*) 500 cc. of dry hydrogen gas at 0° C. and 760 mm.? (*b*) Of 1800 cc.? (*c*) Of 9 l.?

6. The standard pressure at which a gas is measured is 760 mm. Express the same in inches.

7. If 98 gm. of sulphuric acid yield 2 gm. of hydrogen, how many liters of hydrogen (at 0° C. and 760 mm.) can be obtained from 137 gm. of sulphuric acid?

8. How many grams of hydrogen can be obtained (approximately) from 160 gm. of water?

# CHAPTER IV

## Some Properties of Gases

**Introduction.** — Several elements and many compounds are gases or can be readily changed into gases. Elementary gases, besides oxygen and hydrogen, are chlorine and nitrogen; compound gases are carbon dioxide, hydrochloric acid, ammonia, and sulphur dioxide. Air is a mixture of several gases, but it behaves like a single gas. Water is readily converted into the gaseous state, which is familiar as steam and water vapor.

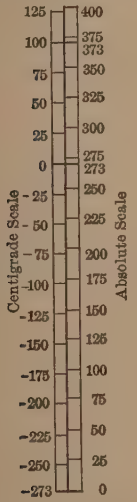
The properties of all gases vary with the temperature and the pressure to which they are subjected. Thus, oxygen gas becomes liquid oxygen at a low temperature, while liquid water is constantly changing into water vapor. The most common and conspicuous change, however, is an alteration in volume whenever pressure and temperature are varied.

**Relation of Gas Volumes to Temperature and Pressure.** — The actual volume occupied by a gas depends upon the temperature and pressure prevailing at the time of observation. The volume expands with rise of temperature or with decrease of pressure; it contracts with fall of temperature or with increase of pressure. In general, if we cool a gas or subject it to a greater pressure, it shrinks; if we heat a gas or subject it to a lower pressure, it expands. By common consent, the normal or standard temperature is zero degrees on the centigrade thermometer (or briefly 0° C.), and the normal or standard pressure is the pressure indicated by the

barometer when the mercury column is 760 millimeters high (or briefly 760 mm.). Under these conditions, which are called **standard conditions**, a liter of dry oxygen gas weighs 1.429 gm. But at another temperature or pressure the liter would contain a different quantity of oxygen gas, and would therefore have a different weight. For example, if the pressure is increased, the volume becomes less, more gas must be added to bring the volume up to a liter, and this second liter of oxygen would weigh more than 1.429 gm. That is, a liter vessel, when full, always contains a liter, but the weight of the contents varies with the quantity of gas contained in this volume. Clearly, if we wish to compare the weights of gases by means of their volumes, we must know the conditions under which the volume is measured. As we shall subsequently see, the comparison of weights of gases is a frequent and highly important operation in chemistry. Some method is necessary, therefore, to permit this comparison. If all gases could be measured at 0° C. and 760 mm., their volumes would be comparable and the weights deduced or obtained directly from these volumes would be a true measure of the actual quantity of the gases in the observed volumes. But it is experimentally inconvenient to measure gases at 0° C. and 760 mm. So it is customary to measure the volume under the conditions existing at the time of the experiment, and then reduce the observed volume to the volume it would occupy under standard conditions. This mathematical reduction is performed by applying two laws, — the law of Charles and the law of Boyle.

**Relation of the Volume of a Gas to Changes in Temperature.** — It has been found by experiment that **all gases under constant pressure expand or contract equally for equal changes of temperature.** More explicitly, a gas

expands or contracts 1/273 of its volume at 0° C. for each degree through which it is heated or cooled. That is, 273 volumes at 0° C. become 274 at 1° C., 275 at 2°, 280 at 7°, 272 at $-1°$, 270 at $-3°$, or in general, $(273 + t)$ volumes at $t°$ (*i.e.* at any temperature). The statement above summarizing the relation between gas volumes and temperature is known as the **Law of Charles.** It applies accurately




| Centigrade | Absolute |
|---|---|
| 200 | 473 |
| 100 | 373 |
| 50 | 323 |
| 25 | 298 |
| 0 | 273 |
| −25 | 248 |
| −50 | 223 |
| −100 | 173 |
| −273 | 0 |

Fig. 6. — Centigrade and absolute thermometer scales (left) and some equivalent degrees (right).

only to the temperature which would ordinarily be used, not to extreme temperatures nor to temperatures near the point at which the gas liquefies. Thus, according to the law, if a gas could be cooled to $-273°$ C., its volume would become zero! But this low temperature has never been reached, and even if it could be, all gases (except possibly helium)

become solid before reaching this temperature. Similarly, many gases dissociate or decompose at very high temperatures, and all deviate from the law when about to change from the gaseous to the liquid state. This point (−273° C.) on the thermometer is called **absolute zero**, and a scale starting at 273° below 0° C. is called the absolute thermometer scale. The relation between the two scales is shown in Figure 6.

An examination of these scales shows that absolute degrees are numerically greater by 273 than the corresponding centigrade degrees. This relation is sometimes expressed by the statement: —

*To convert centigrade into absolute add* 273.

The application of the law of Charles to the reduction of a gas volume to the volume it would occupy at 0° C. can be readily understood by an example. Suppose 10 cc. of dry oxygen gas at 15° C. are to be reduced to the volume occupied at 0° C. The corrected volume, as it is often called, can be found by two processes. (1) The first method utilizes the ordinary centigrade scale. Let the volume at 0° C. be represented by 273. Now since the volume of a gas at 0° C. expands 1/273 for each degree through which it is heated, the volume of oxygen at 15° C. would be represented by 273 + 15. But 273 + 15 and 273 are in the same ratio as 10 (the known volume at 15° C.) and X (the unknown volume at 0° C.). Therefore we can state these relations in a proportion, thus: —

$$273 + 15 : 273 :: 10 : X;\ X = 9.479 \text{ cc.}$$

Therefore, 10 cc. of oxygen at 15° C. occupy 9.479 cc. at 0° C. Since $t$ can be substituted for any temperature (above or below 0° C.), the general form of the proportion can be written: —

$$273 + t : 273 :: \text{known vol.} : \text{vol. at } 0° \text{ C.}$$

(2) The second method uses the absolute scale and is based on the fact that the volumes of a gas at different temperatures vary as their absolute temperatures. Suppose we have 273 cc. of a gas at 0° C. Since it expands 1/273 of its volume at 0° C. for each degree of increase in temperature, and contracts 1/273 for each degree of decrease, its volumes would be as follows for certain centigrade temperatures: —

| Volume in cc. | Centigrade Temperatures |
|---|---|
| 373 | 100 |
| 323 | 50 |
| 273 | 0 |
| 223 | − 50 |
| 173 | − 100 |

Comparing these values with the corresponding absolute temperatures, we have the following relations: —

| Volume in cc. | Centigrade Temperature | Absolute Temperature |
|---|---|---|
| 373 | 100 | 373 |
| 323 | 50 | 323 |
| 273 | 0 | 273 |
| 223 | − 50 | 223 |
| 173 | − 100 | 173 |

It is clear from the first and third columns that the volumes and absolute temperatures are numerically the same. Hence in reducing gas volumes to those occupied at 0° C. by the absolute method, there are three steps. (*a*) Convert the observed centigrade temperature into absolute temperature by adding 273. (*b*) Make 273 the numerator of a fraction and the sum found in (*a*) its denominator. (*c*) Multiply

the given or observed volume by the fraction formed in (*b*). Using the problem given above, the absolute process becomes (*a*) $273 + 15 = 288$, (*b*) $273/288$, (*c*) $10 \times 273/288 = 9.479$. The solution of a few problems by either of these methods will fix in mind the important relation of gas volumes to changes in temperature.

**Relation of Gas Volumes to Changes in Pressure.** — It has been found, by experiment, that **the volume of a gas at a constant temperature is inversely proportional to the pressure.** This statement is the **Law of Boyle**, and was announced by him in 1660. This law, like the law of Charles, applies accurately only to the pressures ordinarily used, but the general numerical relation between volume and pressure as stated above is sufficiently accurate for most purposes. Boyle's law means that the greater the pressure, the less the volume, and *vice versa*. The normal or standard pressure is the mean atmospheric pressure; this is equal to the pressure of a column of mercury 760 millimeters high. Briefly, the normal pressure is 760 mm. Most gases under examination are confined over water or some other liquid whose surface is exposed to the atmosphere, and since atmospheric pressure is transmitted through the liquid to the gas, the pressure which the gas is under is found by reading the pressure recorded by the barometer at the time the gas volume is read. The reduction of the observed volume to the volume it would occupy at 760 mm. is performed by applying Boyle's law. An actual case will make the process clear. Suppose we have 25 cc. of dry oxygen gas at 775 mm. and wish to know its volume at 760 mm. Two processes — not essentially different — can be used. (1) According to Boyle's law, gas volumes are inversely proportional to the pressures; *i.e.* the observed pressure bears the same relation to the normal pressure as the normal

volume bears to the observed volume. This general relation applied to the problem becomes —

$$775 : 760 :: X : 25;\ X = 25.49.$$

Therefore, 25 cc. of oxygen at 775 mm. occupy 25.49 cc. at 760 mm. (2) The other method involves two steps. (*a*) Make 760 the denominator of a fraction and the observed pressure its numerator. (*b*) Multiply the observed volume by the fraction formed in (*a*). Using the same problem, the second process becomes —

$$(a)\ 775/760, \quad (b)\ 25 \times 775/760 = 25.49.$$

**Behavior of Gas Volumes under Simultaneous Action of Heat and Pressure.** — Heat and pressure act independently upon a gas. That is, it is immaterial whether a gas is subjected to heat and to pressure at the same time or in succession. The final volumes are equal in either case. Since both heat and pressure are factors in the cause of the changing gas volume, it is convenient to reduce a gas volume to the standard volume, so to speak, by a single operation. Thus, if the observed volume is 25 cc., the temperature 15° C., and the pressure 775 mm., the standard volume is found thus : —

$$25 \times 775/760 \times 273/288 = X.$$

Sometimes the reduction to standard conditions is performed by substituting the observed values in the formula:

$$V = \frac{V'P'}{760\ [1 + (.00366 \times t)]}.$$

In the formula which merely involves the mathematical operations just described, $V$ = final volume, $V'$ = observed volume, $P'$ = observed pressure, $t$ = observed temperature, and .00366 = 1/273.[1]

[1] The method of deducing this formula is given in the author's "Experimental Chemistry," pp. 361–363.

It should be noted that the reduction of gas volumes to standard conditions is a mathematical process, and does not imply that the gas itself must actually be subjected to these conditions.

**Weight of a Liter of Oxygen Gas.** — As already stated, the weight of a liter of oxygen is 1.429 gm. at 0° C. and 760 mm. Its weight would be different at any other temperature and pressure (unless the effect of heat and pressure balanced each other). This value (1.429) is found by an experiment involving several steps. (*a*) Oxygen is generated from a mixture of potassium chlorate and manganese dioxide, and the quantity liberated is found by subtracting the weight of the oxygen generator after the experiment from its original weight; suppose the weight of liberated oxygen is 2.312 gm. (*b*) The oxygen is collected, its volume noted, and the temperature and pressure also read; suppose the volume of oxygen is 1.75 l., the temperature is 19° C., and the pressure is 755 mm. (*c*) The observed volume is reduced to the volume at standard conditions, thus: —

$$1.75 \times 755/760 \times 273/292 = 1.62.$$

(*d*) The weight of one liter at 0° C. and 760 mm. is then found to be 1.427 gm. by dividing 2.312 (the weight of the oxygen) by 1.62 (the corrected volume of the oxygen), thus: —

$$2.312 \div 1.62 = 1.427.$$

Very accurate experimental work involving precautions not mentioned above yields the value 1.429 gm. as the exact weight of one liter of oxygen.

**Densities of Gases.** — The weight of a liter of many gases can be found by a method similar to that used for oxygen. The values obtained are comparable because the volumes are corrected for temperature and pressure (as reduction

to standard conditions is sometimes designated). Comparison of the weight of a liter of different gases reveals interesting relations. Thus, a liter of air under standard conditions weighs 1.293 gm. Now if we divide 1.429 by 1.293, the quotient (1.105) shows that oxygen is 1.105 times heavier than air. If we divide 1.429 by .08987, which is the weight of a liter of hydrogen at 0° C. and 760 mm., the quotient (15.9) shows that oxygen is 15.9 times heavier than hydrogen. This number (15.9) is the density of oxygen on the hydrogen standard. Density is the relative weight of equal and comparable volumes. Sometimes density is defined as the weight of a body in grams divided by its volume in cubic centimeters. Thus, according to the latter definition the density of oxygen is $1.429 \div 1000 = .001429$. But since in actual practice we more often compare gas volumes with each other, especially with hydrogen or air, the former definition (*i.e.* relative weights of equal volumes) is more convenient. Important deductions are made from the densities of gases, as will appear in a subsequent chapter.

### Problems

1. Reduce the following volumes to the volume occupied at 0° C.: (*a*) 173 cc. at 120° C., (*b*) 466 cc. at 14° C., (*c*) 706 cc. at 15° C., (*d*) 25 cc. at 27° C.

2. Reduce the following volumes to the volume occupied at 760 mm.: (*a*) 200 cc. at 740 mm., (*b*) 25 cc. at 780 mm., (*c*) 467 cc. at 756 mm. *Ans.* (*a*) 194.7, (*b*) 25.65, (*c*) 464.54.

3. Reduce the following to the volume at standard conditions: (*a*) 147 cc. at 570 mm. and 136.5° C., (*b*) 320 cc. at 950 mm. and 91° C., (*c*) 480 cc. at 380 mm. and 68.25° C., (*d*) 25 cc. at 780 mm. and 27° C., (*e*) 14 cc. at 763 mm. and 11° C.

4. Reduce 760 mm. to inches. (See Appendix, § 1.)

# CHAPTER V

## General Properties of Water

WATER is a compound of hydrogen and oxygen, and is worthy of extensive study because of its indispensable relation to life, characteristic properties, and numberless uses.

**Occurrence in Nature.** — Water in the form of vapor is always present in the atmosphere. Evaporation is constantly taking place from the surface of the ocean and other bodies of water, from the moist earth, from the bodies of animals, and from plants. This vapor condenses, and appears as clouds, mist, fog, snow, hail, dew, and frost.

In the liquid state water occurs in vast quantities. About three fourths of the surface of the globe is water. Soil and porous rocks hold considerable, and plants and animals contain a large proportion. Certain substances, which are apparently dry, really retain much water. Thus, in a ton of clover hay there are upwards of 200 lb. of water. Many common foods consist largely of water, as may be seen by the following —

TABLE OF THE PROPORTION OF WATER IN FOOD

| FOOD | PER CENT OF WATER | FOOD | PER CENT OF WATER |
|---|---|---|---|
| Cod | 82.6 | Tomatoes | 94.3 |
| Beef | 61.9 | Apples | 84.6 |
| Lobster | 79.2 | Strawberries | 90.4 |
| Eggs | 73.7 | Watermelon | 92.4 |
| Asparagus | 94.0 | Milk | 87.0 |
| Potatoes | 78.3 | Cheese | 28 to 72 |
| Cucumbers | 95.4 | White Bread | 35.3 |

The human body is nearly 70 per cent water, and during a year the average man drinks about half a ton.

Water in the form of ice permanently covers the coldest parts of the surface of the earth, *e.g.* the polar regions and the summits of high mountains.

**Functions of Water in Nature.** — Since water is the only liquid occurring in large quantities on the earth's surface, it is the most effective agent of **erosion.** It cuts away the earth's crust, and transports the material from higher to lower levels, or washes it ultimately into the ocean. Acting in conjunction with carbon dioxide gas, it decomposes the rocks, changing them into clay, sand, and substances which make the soil productive. The cycle of changes from liquid to vapor and vapor to liquid exerts a marked influence on the distribution of heat and moisture upon the earth's surface, *i.e.* on climate.

Water dissolves many solids and gases, and is constantly extracting from the rocks and soil their soluble constituents, some of which serve for the nutrition of plants, though the larger part passes on to the ocean. The latter thus becomes a vast reservoir of water containing salt and other mineral matter obtained from the earth's crust. In the vital processes of animals and plants water helps change the food into a condition fit for distribution and assimilation.

**Industrial Applications.** — Besides the universal use of water as a beverage, it is applied to an endless variety of useful and convenient purposes. It has always been man's beast of burden. It is the vehicle for transferring mechanical energy to water wheels — an application now being made on a vast scale for generating electricity. It utilizes by its peculiar properties the energy in fuel by means of the steam engine. It is the highway for transportation on the largest scale by ocean, rivers, lake, and canal. It is

the vehicle for the distribution of heat by hot water and steam. It is the indispensable solvent in metallurgy, in the manufacture of many chemicals, and in such industries as soap making, bleaching, brewing, dyeing, and tanning; it is necessary wherever mortar and cement are used. Man's work would be stopped in a thousand other ways were he deprived of water.

**Natural Waters.** — Water is never found pure in nature. Even rain water, which is the purest natural water, contains gases and dust washed from the air. When rain strikes the ground, it begins at once to take up impurities from the rocks and soil. Some of the water flows along the surface, becoming more and more impure, and finally reaches the ocean. But 25 to 40 per cent of the annual rainfall in temperate regions soaks into the ground and percolates through the soil at an estimated rate of .2 to 20 feet a day. On its journey underground the water loses most, often all, of its organic matter (*i.e.* vegetable or animal matter or products of their decomposition), but it dissolves mineral matter and gases. The mineral matter is usually common salt and compounds of calcium and magnesium; the most common gas is carbon dioxide. If the amount of dissolved matter in spring water is large, or the kind of matter is so unusual as to give the water a marked taste or medicinal properties, the water is called **mineral water.** Water containing calcium and magnesium compounds is hard, but in soft water, such as rain water, these compounds are absent.

There are several hundred mineral springs in the United States. Those having a high temperature are called thermal, as at Hot Springs, Arkansas. Many contain a large proportion of common salt, as at Saratoga, New York. Others contain alkaline substances and carbon dioxide gas, *e.g.* Vichy and Apollinaris water. Sulphur springs contain solid or gaseous compounds of sulphur, — or both, — and have

valuable medicinal properties. Some, like Hunyadi, are bitter; but others, especially those in New York State, which contain gaseous sulphur compounds, have a sweet taste but an unpleasant odor. Chalybeate waters contain soluble iron compounds. Many mineral waters contain calcium and magnesium compounds, and a few contain alum and lithium compounds. Most natural mineral waters contain traces of a large number of different substances. Many commercial mineral waters have indifferent medicinal value.

**River water** obviously contains the impurities brought by springs and the surface water; it is also often made very impure by decaying animal and vegetable matter, which has been purposely or accidentally introduced, especially if the river passes through a thickly settled region. A sluggish river is more apt to be impure than a swift one, because the latter tends to purify itself by exposing its impurities to the oxidizing power of the air. **Ocean water** contains a large proportion of common salt. The proportions of the solid substances in their order of abundance are shown in the following —

TABLE OF SOLID SUBSTANCES IN THE OCEAN

| SUBSTANCE | PER CENT | SUBSTANCE | PER CENT |
|---|---|---|---|
| Sodium Chloride . . . | 77.76 | Potassium Sulphate . . | 2.46 |
| Magnesium Chloride . . | 10.88 | Calcium Carbonate . . | .34 |
| Magnesium Sulphate . . | 4.74 | Magnesium Bromide . . | .22 |
| Calcium Sulphate . . . | 3.60 | Other Substances . . . | traces |

The peculiar taste of ocean water is due to the presence of these substances, and since the water only is removed by evaporation, the ocean always has a "salty" taste.

**Drinking Water.** — Water used as a beverage should of course be as pure as possible. As a rule the mineral matter in water selected for drinking is not injurious to health; but since water may become contaminated with

bacteria which produce diseases such as typhoid fever and cholera, it is usually necessary to purify the water before use.

The problem of obtaining suitable drinking water in large quantities is local. The water of many cities is purified by filtering it through a layer of sand and gravel, an acre or more in area and several feet deep. Such a filter removes bacteria almost completely, though it must be frequently cleaned. Sometimes the water is stored in a large settling basin or reservoir and purified by adding alum, or a similar substance, which causes the suspended matter to settle. Ozone is used as a purifier in some localities, and copper sulphate has been applied with varying results to stored water contaminated with certain kinds of organic matter. Dissolved substances cannot be removed without considerable difficulty, so as a rule water is taken from a source which is reasonably pure.

The purity of drinking water is usually determined by a **water analysis**. This is not a decomposition of water, but a chemical examination of a sample for the presence and amount of certain substances which indicate or cause impurity. A chemical examination is of limited value, however, unless it is supplemented by a microscopic study of a fresh sample and a rigid sanitary inspection of the premises. Water which is clear, sparkling, cool, attractive to the eye, and pleasant to the taste may be seriously polluted by disease germs; or it may be liable to sudden contamination from some unsuspected source. On the other hand, a rather unpleasant-looking water may be harmless; hence the necessity of careful and extended examination of water to be used as a beverage.

**The purification of water** on a small scale is accomplished by **distillation**. This operation converts the water and all volatile matter into vapor which is subsequently condensed into the liquid state, but the non-volatile matter dissolved

in the water remains behind in the distilling vessel. It is performed in the laboratory by means of a condenser, which is shown in Figure 7. The condenser consists of an outer tube, *AA*, provided with an inlet and an outlet for a current of cold water, which surrounds the inner tube, *BB*. The vapor from the water boiling in the flask, *C*, condenses in the inner tube, owing to the decrease in temperature,

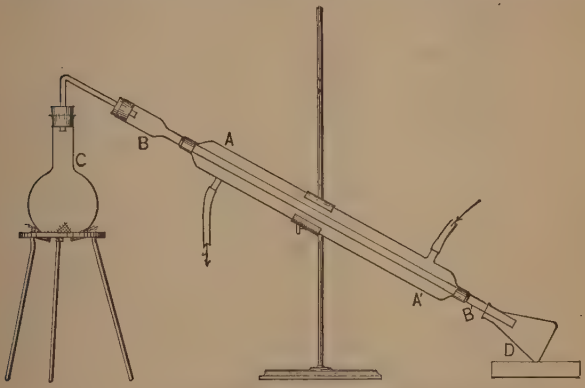



FIG. 7. — Condenser arranged for the distillation of water.

and drops off the lower end of this tube, as the distillate, into the receiver, *D*, while the non-volatile impurities remain behind in the flask. Distilled water is prepared on a large scale in metal vessels, and the vapor is condensed in a block tin pipe coiled inside a vessel through which cold water flows. Distilled water is used in the chemical laboratory; large quantities are made into ice, and considerable (especially after aeration) is used as a beverage. Distillation is one of the processes used to separate liquids from solids and from each other, and finds extensive application in the manufacture of distilled liquors and kerosene oil.

**Physical Properties of Pure Water.** — Owing to its marked solvent power, water is never found pure in nature, and is purified even in the laboratory only by taking special precautions. At the ordinary temperature pure water is a tasteless and odorless liquid. It is usually colorless and transparent, but thick layers are bluish. Water is a poor conductor of heat. This last property can be shown by boiling water near the surface in a large test tube containing a piece of ice weighted down upon the bottom. The ice remains unmelted for some time, although the water is boiling a few inches above it.

Most liquids expand when heated and contract when cooled. Water behaves exceptionally. If water at 100° C. is gradually cooled, it contracts until 4° C. is reached; if the cooling continues, the water expands as long as the liquid state is maintained. Hence at 4° C. a given volume contains the greatest weight of water. In other words, water has its maximum density at 4° C. The density of water at 4° C. is taken as 1; and water at this temperature is the standard for determining the specific gravity of solids and liquids. Thus, when we say specific gravity of gold is 19, we mean that a piece of gold is 19 times heavier than an equal volume of water at 4° C. A cubic centimeter of water at 4° C. weighs 1 gm.

The expansion of water when cooled from 4° C. to 0° C. is slight, but the change is exceedingly important in nature. When the water on the surface of a lake or river cools, it contracts, and since it is heavier (volume for volume) than the warmer water beneath, it sinks. The warmer water rises, becomes cool, and likewise sinks, thus causing a circulation which continues until all the water from the surface to the bottom has a temperature of 4° C. Now if the cooling continues, the surface water expands and remains on the top, because it is lighter than the water beneath

Hence when the temperature of the air falls to 0° C., this upper layer of water freezes and protects the remaining water from the cold air, thus stopping the circulation. Should the circulation continue, as the temperature fell from 4° C. to 0° C., the whole body of water would finally freeze from top to bottom. This condition would not only destroy aquatic life, but profoundly affect climate.

Water solidifies or freezes at 0° C. (or 32° Fahrenheit). And when water freezes, it expands about one tenth of its volume. That is, 100 cc. of water produce about 110 cc. of ice. In other words, 100 cc. of water and 110 cc. of ice weigh 100 gm. each. Hence ice floats. The specific gravity of ice is about .92. The pressure exerted by water when it freezes is powerful. Vessels or pipes filled with water often burst when the water freezes. It is an erroneous but popular idea that "thawing out" a pipe bursts it. As a matter of fact, ice contracts when it melts. The pipe cracks as soon as the water freezes, and when the ice melts a channel is left for the water to flow out of the pipe. Because of this property, ice is an effective agent in splitting rocks. Water creeps into the cracks, especially into narrow ones, by capillary attraction, and when it freezes, the rock splits. Water in freezing also destroys the tissue of living plants, which are often said to have been "touched by frost." Frozen flesh for a similar reason becomes pulpy and is more liable to putrefy when thawed.

Ice melts at 0° C. (32° F.), which is also the freezing point of water. Ice often crystallizes in freezing, but the individual crystals are seldom visible except during the first stages of the process. Snow crystals are common. They are always six-sided, and are formed in the atmosphere by the freezing of water vapor.

Water evaporates at all temperatures, passing off as an invisible vapor into the atmosphere or into the air confined

over it. If water is heated in an open vessel, the temperature rises and vapor passes off rapidly until the thermometer reaches 100° C. (or 212° F.). At this point water boils; *i.e.* it changes rapidly into vapor without rise of temperature. This vapor, if allowed to escape, cools and condenses quickly into a cloud of minute drops of water. This cloud is popularly called steam. Accurately speaking, steam is invisible. What we call steam is a cloud or collection of very small particles of water. This may be illustrated by boiling water in a large glass flask. The inside of the flask is perfectly transparent, although there is a cloud of "steam" issuing from its mouth.

The evaporation of water has important scientific application. If a little water is introduced into a dry closed

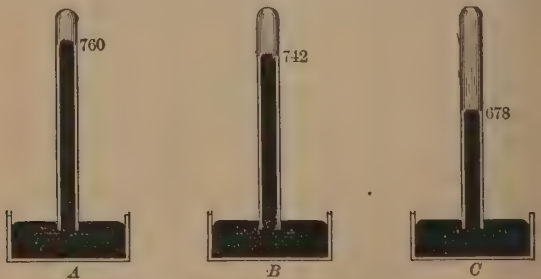



Fig. 8. — Varying vapor pressure.

bottle having a U-shaped tube of colored liquid connected with the interior to serve as a gauge, the difference in the levels of the colored liquid indicates a pressure inside the bottle. This pressure is due to the vapor which escapes from the water. The ability of water to produce and maintain a pressure by its vapor is called the **vapor tension** of water. The opposing pressure exerted by the vapor is called the **vapor pressure** of water vapor, and it depends

upon the temperature of the water. This is readily seen by comparing the heights of the mercury in the barometer tubes shown in Figure 8. In the tube *A* there is no water vapor in the space above the mercury, and therefore the height of the mercury is 760 mm. In the tube *B* the space above the mercury is filled with water vapor at 20° C.; the vapor exerts a pressure and forces the mercury down to nearly 742 mm. That is, the water vapor at 20° C. exerts a pressure equal to about 18 mm. of mercury. Similarly, in the tube *C* the space is filled with water vapor at 50° C. and the mercury is forced down to 678 mm., the water vapor exerting a pressure of about 82 mm. If the vapor were at 0° C., the vapor pressure would be about 4.5 mm., and at 100° C. the vapor pressure would be 760 mm. The latter value is instructive, for it means that at the boiling point of water (100° C.) the vapor pressure just balances the normal atmospheric pressure. The pressure exerted by water vapor, as shown in Figure 8, is independent of atmospheric pressure, the size and shape of the inclosing space, and the pressure of other gases. It depends solely upon the temperature of the evaporating water, and has a maximum value for each temperature. These values have been carefully determined by experiment, and can be found in the Table of Vapor Pressure given in the Appendix, § 4.

A practical application of vapor pressure is made in determining the weight of a liter of oxygen and in similar experiments where gases are measured over water. The oxygen gas is collected in a bottle or graduated tube inverted in a vessel of water. If the gas is allowed to stand confined over the water long enough, it becomes saturated with water vapor ; *i.e.* the tube finally contains a mixture of oxygen and the maximum amount of water vapor at the given temperature. In such a mixture, where no chemical action occurs, each gaseous constituent shares the total pressure

(against the atmospheric pressure). This proportionate part of the total pressure is called the partial pressure of that gas. If the oxygen were confined over mercury, its pressure would be the same as its partial pressure when saturated with water vapor. Hence the actual pressure under which the oxygen itself exists is found by determining its partial pressure or by subtracting the partial pressure of the water vapor from the total pressure (indicated by the barometer). The latter method is used, because the pressure of water vapor at any temperature is known and can be taken directly from the table. Incorporating this fact into the formula given in Chapter IV for reducing the volume of a gas to its volume at 0° C. and 760 mm. the formula becomes —

$$V = \frac{V'(P' - a)}{760\ [1 + (.00366\ t)]}.$$

In this formula $V$ means the volume of dry oxygen at 0° C. and 760 mm., and $a$ means the vapor pressure (found in the table in the Appendix, § 4).

Several important conclusions can be drawn from the discussion of vapor pressure in the foregoing paragraphs. Recalling the fact that the vapor pressure of water at 100° C. is 760 mm., it is obvious that this temperature is the boiling point at this pressure. Water boils when its vapor escapes with sufficient pressure to overcome the pressure upon its surface. Hence the boiling point depends upon the pressure — either of the atmosphere or of the vapor in the vessel. The **boiling point** of water is 100° C. (or 212° F.) only when the atmospheric pressure is normal, *i.e.* 760 mm. The boiling point becomes lower as the pressure is decreased and higher as the pressure is increased. For example, in the city of Mexico (7500 ft. above the sea level) water boils at 92° C., and in Quito (9350 ft. above the sea level) water

boils at about 90° C. Again, the condition in a closed vessel containing water and water vapor merits consideration. As the water evaporates, the vapor pressure increases until the space above the water becomes saturated with water vapor. Then the vapor pressure remains constant as as long as the temperature is fixed, say 20° C. The vapor tension of the water is now equal to the vapor pressure of the vapor. In other words, vapor tension and vapor pressure balance each other. Vapor is condensing, however, just as fast as water is changing into vapor. Such a condition of mutual exchange is called a state of **equilibrium**, *i.e.* a condition in which two opposing processes balance but do not stop each other. Equilibrium is approached or reached in many processes, chemical as well as physical.

**Chemical Properties of Water.** — Water has such conspicuous physical properties that its chemical properties are sometimes ignored or discussed in connection with other substances. Such discussion, it must be admitted, is often more appropriate elsewhere, but certain phases of this topic need attention here. Water at the ordinary temperature interacts with certain metals, especially sodium and potassium. This chemical change, as already stated, is substitution. The metal is substituted for part of the hydrogen of the water, thereby liberating hydrogen and producing a new compound, which contains sodium, hydrogen, and oxygen, and is called sodium hydroxide. Magnesium and zinc interact similarly with boiling water, the products being hydrogen, magnesium hydroxide, and zinc hydroxide. Water is decomposed to some extent into its component elements (oxygen and hydrogen) by intense heat; at about 2000° C. the decomposition is less than 2 per cent. As the temperature falls, the elements recombine to form water. Both decomposition and recombination

are gradual. Water when decomposed by heat behaves differently from potassium chlorate. The latter compound suffers permanent decomposition; *i.e.* the oxygen and the potassium chloride into which it is decomposed do not recombine as the temperature falls. It is customary to distinguish these two kinds of decomposition. That kind which takes place gradually at high temperatures and is followed by recombination when the temperature is lowered is called **dissociation by heat.** Several common compounds undergo dissociation when heated, and they will be discussed later. Water is decomposed when heated with certain metals, *e.g.* iron, but the oxygen at once combines with the metal, so the final products are hydrogen and an oxide of the metal. A mixture of water and sulphuric acid yields hydrogen and oxygen when subjected to the action of an electric current. Apparently the water is merely decomposed into its elements, but it will be shown subsequently that the action is not so simple. (See Chapter IX.) Water combines directly with many oxides. Thus, lime, which has the chemical name calcium oxide, combines directly with water and forms a compound called calcium hydroxide. Similarly, barium oxide forms barium hydroxide, sulphur dioxide forms sulphurous acid, phosphorus pentoxide forms phosphoric acid. These chemical changes may be typically represented thus :—

Calcium Oxide + Water = Calcium Hydroxide.
Sulphur Dioxide + Water = Sulphurous Acid.

A chapter will be devoted to these resulting compounds. (See Chapter X.) Water also combines with certain solids when they separate from a solution by crystallization. Thus, copper sulphate crystals are blue, but when heated, water is liberated and the crystals crumble to a gray white powder. This class of compounds, in which water is a

definite component, is treated below. (See in this chapter Solution and Crystallization.)

**Solvent Power of Water.** — This is one of the most conspicuous properties of water and can be discussed from several standpoints. Only the simpler physical aspects are treated in this chapter. More extended discussion may be found in Chapter IX.

Daily experience shows that many solids, liquids, and gases disappear when put into water. This operation is called dissolving or putting into solution. The clear, transparent liquid containing the dissolved substance is called the **solution.** The liquid in which the substance dissolves is called the **solvent,** and the dissolved substance is called the **solute.** If the solute is not volatile, or not very volatile, it can be recovered by evaporating, or distilling off, the water. The degree of solubility of a substance is often conveniently expressed by the terms slightly soluble, soluble, and very soluble. It is more accurate, however, to state the proportions of the solvent and the solute, and also the temperature. Thus, instead of saying that common salt is very soluble in cold water, it is better to state that 36 gm. of salt dissolve in 100 gm. of water at 20° C. There is a limit to the weight of each substance which a given weight of water will dissolve. That is, substances differ widely in the degree of solubility. Some, like potassium permanganate, are very soluble, while others, like sand, dissolve only very slightly. The latter class is often said to be insoluble. Strictly speaking, no substance is insoluble, but the term is often applied to those substances whose solubility is so slight that it can be neglected in most cases. Many minerals and rocks belong to the class of so-called insoluble substances.

The concentration of a solution is its strength as de-

termined by the amount of solute dissolved in a given amount of solvent. The ratio of these two amounts expresses the concentration. A solution which contains a small proportion of solute is called a **dilute solution**, or one of small concentration; one containing a large proportion of solute is called a **concentrated solution.** Thus, dilute sulphuric acid usually contains one part of acid to three or more parts of water, while concentrated sulphuric acid is nearly 98 per cent acid. Sometimes the terms *weak* and *strong* are used instead of *dilute* and *concentrated.* Other terms are defined below. (See Solubility of Solids.)

√ **Solution of Gases.** — Water dissolves many gases. The solubility varies widely. For example, one volume of water dissolves about 1150 volumes of ammonia gas (at 0° C. and 760 mm.), 550 of hydrochloric acid gas, 80 of sulphur dioxide gas, 1.8 of carbon dioxide gas, .04 of oxygen, .02 of nitrogen, and .02 of hydrogen.

As a rule the volume of gas dissolved by a given volume of water decreases with rise of temperature. Thus, when ammonium hydroxide is heated, ammonia gas escapes freely. So also, when water is heated gradually, the air dissolved in the water gathers as little bubbles, which soon rise and escape. Again, 100 volumes of water dissolve approximately 4 volumes of oxygen at 0° C., 3 at 20° C., 1.8 at 50° C., and none at 100° C. The complete removal of a gas by boiling its solution is not possible in the case of certain very soluble gases, like hydrochloric acid gas. Probably there is a chemical combination to some extent between the solvent and the solute when very soluble gases dissolve in water. (See Hydrochloric Acid.)

Pressure influences the solubility of gases. Thus, large quantities of carbon dioxide gas are forced into cylinders full of water in preparing soda water. When the pressure

is removed, the gas escapes rapidly and causes the soda water to froth or foam. This rapid escape of gas is called effervescence. Underground waters often contain large amounts of gases, especially carbon dioxide, owing to the great pressure to which subterranean gases are subjected. Hence, mineral waters often effervesce when they come to the surface. The greater the pressure, the greater the amount of gas dissolved. More accurately stated, the weight of a moderately soluble gas dissolved by a given weight of water is directly proportional to the pressure, if the temperature is constant. This is one form of the general statement known as **Henry's Law.** Gases which are very soluble or which dissolve under great pressure deviate from this law, probably owing to chemical combination. (See also preceding paragraph.)

When a mixture of gases, such as air, dissolves in water, each ingredient behaves independently of the other. More strictly, each gas dissolves proportionally to its partial pressure. For example, the ratio of oxygen to nitrogen in air is about 1:4 and the ratio of their solubilities when not mixed is 2:1, but the ratio of oxygen to nitrogen in water saturated with air (at 760 mm.) is 7:13 or about 1:2. The difference is due to the fact that their solubility when mixed is determined not merely by their power to dissolve as free gases but also by their partial pressure.

**Solutions of Liquids.** — The solubility of liquids in water varies between wide limits. Some, such as alcohol and glycerine, are soluble in all proportions. Oils, such as kerosene, are practically insoluble; hence the old adage, "Oil and water will not mix." Carbon disulphide is also almost entirely insoluble, as is shown by the fact that after agitation with water it separates almost entirely as a distinct layer; being heavier than water, this layer forms at the

bottom. The mere formation in this way of separate layers by two liquids must not be accepted as evidence of their insolubility. Only in those cases which exhibit perfect mutual solubility is the separation into layers after agitation impossible. Ether and water form two layers, but each dissolves appreciably in the other. Thus, about 2 gm. of ether dissolves in 100 gm. of water (at 20° C.) and about 10 gm. of water dissolves in 100 gm. of ether. The upper layer consists of ether saturated with water; the lower, of water saturated with ether. Alcohol and water form no such layers, not because each is soluble in the other, but because each is soluble without limit in the other ; *i.e.* it is a case of perfect mutual solubility. In many cases a rise in temperature increases the solubility of liquids in water.

**Solutions of Solids.** — The solubility of solids in water is a subject of much practical importance. The abundance of water and its power to dissolve such a vast number of different solids have led some to call water " the universal solvent." The far-reaching effect of this marvelous power in nature and the indispensable value of water to man have been considered. (See above.)

The degree of solubility of solids in water depends upon the substance itself and the temperature of the water. Some solids are very soluble, while others are difficultly soluble. In most cases solubility increases with a rise of temperature ; hence the common practice of heating to hasten solution. The effect of an increase of temperature on solubility is sometimes very marked, the solubility being increased many fold in passing from the ordinary temperature to the boiling point. A few solids (*e.g.* calcium hydroxide) are less soluble in hot water than in cold, and a few others (*e.g.* sodium chloride) dissolve to about the same degree in hot and cold water. These properties of the solutions of various solids are illustrated by the following —

TABLE OF THE SOLUBILITY OF SOLIDS IN WATER

| SOLIDS | NUMBER OF GRAMS IN SOLUTION IN 100 GRAMS OF WATER | |
|---|---|---|
| | 20° C. | 100° C. |
| Calcium Chloride | 74 | 155 |
| Copper Sulphate (cryst.) | 42.3 | 203.3 |
| Magnesium Sulphate | 36.2 | 73.8 |
| Potassium Chlorate | 7.2 | 59.5 |
| Potassium Chloride | 35 | 57 |
| Potassium Dichromate | 13 | 102 |
| Potassium Nitrate | 31.7 | 246 |
| Potassium Sulphate | 10.6 | 26 |
| Sodium Chloride | 36 | 39.7 |

Other facts about the solubility of solids are illustrated by this table besides the dependence on the substance itself and on temperature. Inspection of the table shows that there is a limit to the solubility of solids in water at a given temperature. That is, a given weight of water at a fixed temperature will dissolve a definite weight of solid and no more, even though more *undissolved* solid may be available. A solution conforming to the conditions just stated is said to be **saturated** or to have reached its **maximum concentration**. Thus, 100 gm. of water holds 7.2 gm. of potassium chlorate in solution at 20° C. If more potassium chlorate is added, it remains undissolved (provided the temperature of the solution and the weight of water are unchanged). If the temperature falls, more solid comes out of solution; and conversely, if the temperature rises, more solid dissolves. As long as the maximum concentration is maintained in contact with some of the undissolved solid, the solution is saturated. The ratio of the weight of the solute to the weight of the solvent in a saturated solution is called the **solubility** of the solid. It is customary in expressing solubility to

represent the amount of solvent by 100 gm.; on this basis the solubility of a solid becomes the number of grams of solid dissolved by 100 gm. of water. In the case just cited, the maximum concentration, or, as it is more often called,

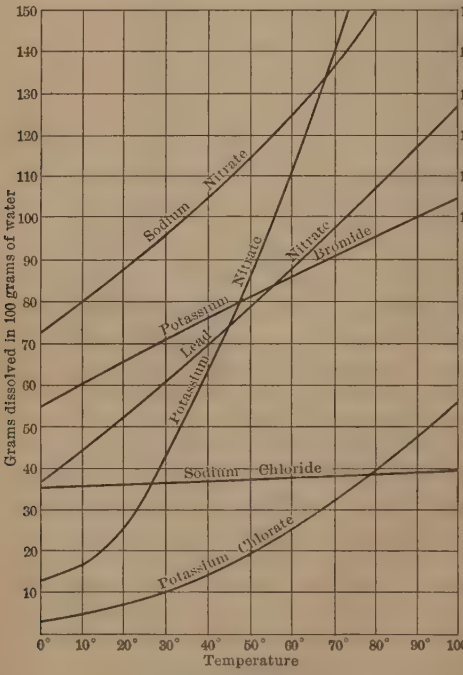

Grams dissolved in 100 grams of water
Temperature
Sodium Nitrate
Potassium Nitrate
Lead Nitrate
Potassium Bromide
Sodium Chloride
Potassium Chlorate
0° 10° 20° 30° 40° 50° 60° 70° 80° 90° 100°
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

Fig. 9. — Solubility curves.

the solubility, of potassium chlorate is 7.2 gm. at 20° C. and 59.5 gm. at 100° C.

The table of solubilities just given is limited to two temperatures. A convenient way of showing the solubility of

a substance as the temperature varies between convenient points is by a solubility curve. The curves of several substances are shown in Figure 9. The temperatures are read from the vertical lines and the number of grams of solute in 100 gm. of water is read from the horizontal lines. For example, if we wish to know the temperature at which 40 gm. of potassium chlorate are held in solution by 100 gm. of water, it is only necessary to find where the horizontal line numbered 40 cuts the potassium chlorate curve, and then follow the vertical line down to the temperature numbers, where 80° C. is found. Similarly, 100 gm. of water dissolve 37 gm. of sodium chloride at 60° C., while the same weight of water dissolves 110 gm. of potassium nitrate at 60° C., and so on.

When hot solutions are cooled or concentrated solutions are evaporated, the solute separates in the solid state just as soon as the saturation point (at a lower temperature) is passed. Under certain favorable conditions the solid is deposited in masses having a definite form. These masses are called **crystals** and the process of obtaining them is called **crystallization.** The form and color of the crystals are characteristic of the particular substance and serve to identify it. Thus, potassium chlorate crystallizes in shining white plates or leaves, and common salt in white cubes. The deposition of crystals is not always as prompt as just stated. Thus a hot, saturated solution of some solids, such as sodium sulphate and sodium thiosulphate, deposits no crystals when the clear solution cools. Such solutions are called **supersaturated.** Supersaturation can occur only when the undissolved solid is not present. If a fragment of the solid is dropped into the supersaturated solution, crystals very soon begin to form upon the fragment, and this separation continues until just enough solid is left in solution to produce saturation at the prevailing temperature. The

amount of solid thus separated is often very great and sometimes forms a solid mass in the test tube.

It is evident from the foregoing paragraphs that there are three general classes of solutions of solids, viz. unsaturated, saturated, and supersaturated. These classes can be distinguished by bringing each in contact with more of the solid. If the solution is unsaturated, more solid will dissolve; if saturated, no more will dissolve; if supersaturated, solid will be deposited until saturation is reached. In an unsaturated solution the concentration is less than in a saturated solution, while in a supersaturated solution it is greater. If we think of these solutions as being in contact with a solid, their relations will be clearer than if we regard them as reservoirs, so to speak, for more or less solid. In the saturated solution there is equilibrium between the solution and the solid. That is, there is an equal tendency for the solid to enter and to leave the solution. But in the other two solutions no such equilibrium prevails, for the unsaturated solution takes up more solid and the supersaturated solution deposits solid; both are stable when solid is absent, but unstable as soon as solid is present.

**Solution and Crystallization.** — Under the chemical properties of water it was stated that water combines with certain solids when they are separated from a solution by crystallization. Crystals deposited from solutions often contain water, which is an essential part of the compound. The combined water must not be confused with water which adheres to a crystal or is inclosed in it. Even after the crystals are powdered and dried, the combined water remains, which can be removed by heat or sometimes merely by exposure to the air. Loss of water is sometimes attended by loss of color and always by loss of crystalline appearance. Thus, crystallized sodium carbonate turns dull and crumbles

in the air; blue crystallized copper sulphate turns white slowly at the ordinary temperature and very rapidly when heated, finally becoming a gray powder; but the variety of crystallized gypsum called selenite must be heated before the combined water passes off, whereupon the crystal becomes chalky and crumbles when compressed. The proportion of combined water in crystals is not arbitrary. It is constant in the same compound when crystallized under uniform conditions. The amount in different substances varies between wide limits, as can be seen by the following —

TABLE OF COMBINED WATER IN CRYSTALS

| CRYSTALLIZED SOLID | PER CENT OF COMBINED WATER |
|---|---|
| Barium Chloride . . . . . | 14.75 |
| Copper Sulphate . . . . . | 36.36 |
| Iron Sulphate . . . . . | 45.35 |

There is no doubt that the water in the crystallized form of compounds is not chemically combined in the way the other elements are; for when such crystals are heated with proper precautions, only the water is removed, the other constituents of the original compound remaining intact. In most cases gentle heating suffices to expel the water. Hence the combination between the water and the rest of the compound must be weaker than that between the constituents of the residue or at least of a different order. This fact is often indicated by separating the water in the formula; *e.g.* $CuSO_4 . 5\,H_2O$ and $BaCl_2 . 2\,H_2O$. Water chemically combined in a crystal and readily removed in a definite proportion by heating is called **water of crystallization**. Compounds containing water of crystallization are sometimes called **hydrates** or hydrated compounds. Conversely, compounds which have been deprived of water of crystallization are said

to be **anhydrous** or dehydrated. For example, blue crystallized copper sulphate is a hydrate of the compound copper sulphate $CuSO_4$, but when the blue compound is heated, it becomes anhydrous or dehydrated copper sulphate, which is a gray powder. Anhydrous compounds often readily become hydrated again. Thus, when the gray anhydrous copper sulphate is added to water, a blue solution is produced from which blue crystals of hydrated copper sulphate are readily obtained.

Some substances give up their water of crystallization wholly or in part upon mere exposure to the air; such substances are said to be efflorescent or to effloresce. Thus, sodium carbonate crystals when left in the air become opaque and ultimately crumble, owing to the slow escape of their water of crystallization. The white spots often seen on blue crystals of copper sulphate or on green ones of iron sulphate are due to **efflorescence**. An explanation of efflorescence is found in the principle of vapor pressure. Substances containing water of crystallization exert a vapor pressure. If this vapor pressure is greater than the pressure of the water vapor in the atmosphere, the substance loses water until the vapor pressures are equal or until all the water has escaped from the substance. Hence, in general, all hydrated compounds effloresce, if they exert a vapor pressure greater than that of the atmosphere (at that time).

It should not be concluded from the foregoing statements that all crystallized solids which dissolve in water contain water of crystallization. Many do not; *e.g.* sodium chloride, potassium chlorate, sugar, potassium nitrate, and potassium dichromate. No satisfactory explanation has been given for the absence of water of crystallization in certain crystallized compounds; nor for the varying amount and relation to color and crystal form in hydrated compounds.

The formation of crystals is not limited to a single process,

viz. cooling or evaporating a solution. It can be accomplished by fusion and by sublimation. Thus, sulphur crystallizes when melted (or fused) and then cooled, and iodine crystallizes when vaporized and then cooled. These processes of obtaining crystals are called respectively evaporation, fusion, and sublimation. All three will be illustrated in succeeding chapters. As a rule crystals obtained by any of these methods are quite pure, and crystallization is one of the processes frequently used in the industrial preparation of chemicals. A crystal is "a solid body bounded by plane surfaces arranged according to definite laws, and possessing definite physical properties; both external form and physical properties resulting from, and being the expression of, definite internal structure." The external form is the most conspicuous characteristic of a crystal, and, as a rule, each substance has a crystal form or series of closely related forms by which it can be distinguished. Thus, salt crystallizes in cubes, alum in octahedrons, sulphur in orthorhombic forms, and calcite (calcium carbonate) in hexagonal forms. Many minerals occur as crystals, and since they are the natural form of chemical compounds as well as the source of many elements, a knowledge of the common crystal forms and the properties of crystals is indispensable in identifying substances and interpreting descriptions. Such knowledge is best acquired by a constant examination of crystals. The preliminary treatment given in the Appendix, § 3, will serve as an introduction to this important subject.

**Solution and Vapor Pressure.** — Aqueous solutions have a vapor pressure, but it is less than the vapor pressure of water at the same temperature. This fact can be illustrated by introducing a solution into the barometer tube as described under vapor pressure. Under parallel conditions the mercury will always stand higher in the tube containing the

solution, *i.e.* the vapor pressure is less, and consequently the mercury will be less depressed. Several conclusions can be drawn from this fact. Since the boiling point depends upon pressure, solutions must be heated to a higher temperature than water before boiling occurs. That is, a solid dissolved in water elevates the boiling point of water. Moreover, the elevation of the boiling point depends in general upon the weight of solid dissolved in a given weight of water ; *i.e.* it is proportional to the concentration of the solution. This means that if the weight of solute is doubled, the elevation of the boiling point is doubled. Similar statements can be made about the freezing point of solutions. The freezing point of a solution is lower than the freezing point of water, and the depression of the freezing point is proportional to the concentration of the solution. Important deductions will subsequently be made from these relations. In passing, it is interesting to note two common illustrations of the foregoing statements, viz. that boiler water containing much dissolved solid has to be heated to a higher temperature than pure water in the production of steam, and that the salt water along the seashore freezes, if at all, with more difficulty than the fresh water of near-by rivers. Finally, the relatively lower vapor pressure of solutions explains the deliquescence of certain substances. Many substances absorb water when exposed to the air, become moist, and sometimes even dissolve in the absorbed water. Calcium chloride, potassium carbonate, zinc chloride, sodium hydroxide, magnesium chloride, and potassium hydroxide belong to this class. This property is called **deliquescence**, and the substances are said to deliquesce, or to be deliquescent. Deliquescence is a property of very soluble substances. Water vapor from the air condenses on the surface and produces a very concentrated solution, which has a vapor pressure much lower than the average pressure of the water

vapor in the air. The solution, therefore, continues to take up water until its vapor pressure equals the partial pressure of the water vapor in the air. Common salt, or sodium chloride, often deliquesces, especially in damp weather. The deliquescence is due, however, to the presence of magnesium and calcium chlorides. Sodium nitrate is somewhat deliquescent, and is not usually used in the manufacture of gunpowder; potassium nitrate, which is not deliquescent, is used instead. This property of deliquescence is often utilized in the laboratory to remove water vapor from gases, calcium chloride being usually employed for this purpose. Substances thus used are often called drying or desiccating agents.

**Thermal Phenomena of Solution.** — The process of solution is often accompanied by an appreciable change of temperature. Thus, when sulphuric acid is poured into water, heat is liberated. With relatively large quantities of acid the heat is so great that the mixture often boils, and sometimes the hot acid is spattered. Hence, the acid should be added slowly to the water, and the mixture constantly stirred. Other substances which dissolve with the liberation of heat are fused calcium chloride, potassium hydroxide, and sodium hydroxide. Some substances which dissolve with a fall of temperature (*i.e.* with absorption of heat) are crystallized calcium chloride, ammonium nitrate, ammonium chloride, and potassium nitrate. The final result of the entire act of solution is doubtless due to several factors. One of these is the change in volume of the solute. Thus, a very soluble gas becomes greatly condensed, while a solid, on the other hand, occupies a much larger volume after solution than before. Another important factor is chemical action between the solute and solvent. The heat liberated or absorbed during the process of solution is called **heat of solution**. This rather complex subject is still under investigation.

**Solution and Chemical Action.** — When a substance dissolves, it is so modified that it can participate more readily in chemical changes. Hence, solution is an aid to chemical change. Thus, if dry tartaric acid and sodium bicarbonate are mixed, there is no evidence of chemical action; but when the mixture is poured into water, the copious evolution of carbon dioxide gas is conclusive evidence of a chemical change. Similarly, when a dry mixture of ferrous sulphate and potassium ferrocyanide is poured into water, the immediate appearance of a blue precipitate shows that water was needed for the chemical change. Solution is such an important aid to chemical action that many substances employed in the laboratory are in solution, and many processes in chemistry are "wet" processes.

**The Nature of Solution** has long been a subject of speculation and study. The problem as a whole is still unsolved, though much light has been thrown upon the question by recent investigations. (See Chapter IX.)

### Problems

1. If 1.5 gm. of crystallized barium chloride loses .22 gm. when heated to constant weight, what per cent of water of crystallization does it contain? 14.87

2. If 2 gm. of another lot of barium chloride loses .295 gm., what per cent of it was water of crystallization?

3. A tube contains 97.2 cc. of gas at 20.3° C. and 756 mm., and the vapor pressure is 17.65. What is the volume of the dry gas at 0° C. and 760 mm.?

4. Reduce the following as in Problem 3: (*a*) 77 cc., 17.5° C., 755 mm., 14.89 *a*; (*b*) 81.2 cc., 746.8 mm., 19.5° C., 16.87 *a*; (*c*) 100 cc., 755.3 mm., 18.5° C., 15.85 *a*.

5. If the density of ice is .92, what volume will a liter of water at 4° C. occupy when frozen? *Ans.* 1.087 l.

6. How much water (approximately) is contained in (*a*) 2 lb.

of lobster, (*b*) 56 lb. of potatoes, (*c*) 1 lb. of tomatoes, (*d*) 2 lb. of milk, (*e*) 1 lb. of white bread, (*f*) a human body weighing 150 lb.?

7. If crystallized calcium sulphate contains about 18 per cent of water, what volume of steam at 200° C. and 755 mm. is given off by heating 100 gm. of the solid until all the water of crystallization is expelled?

## CHAPTER VI

### Composition of Water — Hydrogen Dioxide

WATER was called an element until about the end of the eighteenth century. At that time it was shown to be a compound of hydrogen and oxygen. Since water is the first chemical compound we are to study, special attention will be paid to its typical characteristics.

We should recall at this point the essential characteristic of a chemical compound, viz. its constituents are elements chemically combined in a fixed ratio by weight.

**The Composition of a Compound** is determined either by analysis or synthesis, *i.e.* by taking it apart or putting its parts together. Sometimes both methods are used, since each fortifies the other and strengthens the final conclusion. These methods find excellent application in determining the composition of water. Analysis and synthesis may be qualitative or quantitative. A qualitative experiment is a study of compounds with a view of discovering what elements or groups of elements they contain. A quantitative experiment is an accurate determination of the weight or volume of the constituents of a compound. Obviously, a complete study of the composition of a compound requires both kinds of tests, the qualitative as a rule preceding the quantitative.

**Water contains Hydrogen.** — When steam is passed over heated metals, hydrogen is liberated. Lavoisier's demonstration of this fact has already been considered (see Preparation of Hydrogen). The fact that sodium liberates hydrogen

from water at the ordinary temperature has also been discussed (see *ibid.*). If red litmus paper is put into the water from which the sodium has liberated hydrogen, the litmus paper becomes blue. This change of color from red to blue shows that an alkali is in the water, because alkalies turn red litmus paper blue. The alkali is sodium hydroxide, and it may be obtained as a white solid by evaporating the water. Sodium hydroxide is a compound of sodium, hydrogen, and oxygen, and is formed by replacing half of the hydrogen of water by sodium. Since sodium liberates hydrogen from water, and forms at the same time a compound — sodium hydroxide — containing hydrogen, the hydrogen in water must be divisible into two parts. Now if .1 gm. of sodium is allowed to act upon water, 48.22 cc. of hydrogen are liberated; and if the sodium hydroxide thus formed is dried and heated with sodium, 48.22 cc. more of hydrogen are obtained. This shows that the hydrogen in water is divisible into two equal parts — a fact of fundamental importance.

**Water contains Oxygen.** — The fact that oxygen is a constituent of water has already been suggested; *e.g.* (1) by the production of water when hydrogen is burned in air, (2) by the formation of a compound of iron and oxygen when steam is passed over hot iron, and (3) by the formation of sodium hydroxide when sodium interacts with water. These proofs, however, are indirect. A simple direct demonstration of the presence of oxygen in water can be made by allowing chlorine water to stand in the sunlight. (Chlorine water is prepared by saturating water with chlorine gas — an element to be studied in Chapter XII.) A tube about a meter long is completely filled with chlorine water, the open end is immersed in a vessel containing the same solution and the whole apparatus is placed in the direct sunlight. Bubbles of gas soon appear in the liquid, and after a few

hours a small volume of gas collects at the top of the tube. This gas can be shown to be oxygen by the usual test, viz. relighting a glowing splinter of wood.

**Decomposition of Water.** — When steam is heated to a very high temperature (about 2500° C.), it decomposes to a very slight extent into hydrogen and oxygen. This method, however, is not as convenient as the one in which an electric current is used. The decomposition of water by electricity is called traditionally the electrolysis of water, though we shall see later (Chapters IX and XI) that the process is more complex than the apparent disruption of water into hydrogen and oxygen. The operation is accomplished in a special form of apparatus devised by Hofmann and shown in Figure 10. Pure water does not conduct electricity, so a mixture of water (10 vols.) and sulphuric acid (1 vol.) is poured into the apparatus until the reservoir is half full after the stopcocks have been closed. As soon as an electric battery of three or more cells is connected by wires with the piece of platinum near the bottom of each tube, bubbles of gas gather on the platinum, and as the action proceeds, the bubbles rise, collect in the upper part of the tubes, and slowly force the liquid from each tube into the reservoir. The volume of gas is greater in one

FIG. 10. — Hofmann apparatus for the electrolysis of water.

tube. Assuming that the tubes have the same diameter, the volumes are in the same ratio as their heights, which will be found by measurement to be approximately two to one. Appropriate tests show that the gas having the larger volume is hydrogen and the one having the smaller volume is oxygen. Many accurate repetitions of this experiment have shown that only hydrogen and oxygen are produced, and that the volume of the hydrogen is twice that of the oxygen.

Water was first decomposed by electricity in 1800 by Nicholson and Carlisle. Davy confirmed their work by a series of brilliant experiments extending through a period of six years (1800–1806).

**The Quantitative Composition of Water.** — Decisive evidence of the quantitative composition of water is obtained by a determination of its volumetric and its gravimetric composition. Volumetric means "by volume" and gravimetric means "by weight."

**The Volumetric Composition of Water** is determined by exploding a mixture of known volumes of hydrogen and oxygen in a eudiometer. It is a method of synthesis.

A simple sketch of a convenient form of apparatus for determining the volumetric composition of water is shown in Figure 11. The essential part is the eudiometer, *F*. In this glass tube the gases are accurately measured and exploded.

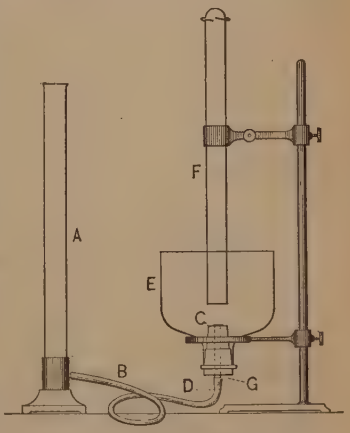



Fig. 11. — Apparatus for determining the volumetric composition of water.

The electric spark which causes the explosion is obtained from an induction coil and battery. The spark leaps across the space between the platinum wires at the top of the inside of the eudiometer, and the heat produced by this spark causes the hydrogen and oxygen to combine and form water. Omitting details, oxygen and hydrogen are introduced separately into the eudiometer and measured and the mixture is then exploded; after the explosion, which is indicated by a slight click or flash of light, water from the reservoir, *E*, rushes up into the eudiometer. The water does not completely fill the eudiometer, because an excess of one gas was added. This additional gas takes no part in the chemical change, but merely serves to lessen the violence of the explosion, which otherwise might break the eudiometer. The quantity of water formed by the union of the hydrogen and oxygen is too minute to measure. A concrete illustration will make the process more intelligible. Suppose the volumes of the participating gases after reduction to standard temperature and pressure and the dry state are as follows : —

| | |
|---|---|
| Vol. of hydrogen added . . . . . | 32.4 cc. |
| Vol. of oxygen added . . . . . | 12.3 cc. |
| Vol. of residual hydrogen . . . . . | 7.8 cc. |

The actual volume of hydrogen which combined with all the oxygen is 24.6 cc. (*i.e.* 32.4 − 7.8). Therefore the two gases combined in the ratio of 24.6 to 12.3, or 2 to 1; or, as it is usually stated, two volumes of hydrogen combine with one volume of oxygen to form water. The ratio based on the most painstaking work is given as 2.0027 to 1.

The discovery of the volumetric composition of water was not made by any one chemist. Priestley, about 1780, noticed that when a mixture of air and hydrogen was exploded, "the inside of the glass, though clear and dry before, immediately became dewy." Cavendish,

in 1781, showed that when a mixture of two parts hydrogen and one part oxygen was exploded, nothing but water was formed. Watt, in 1783, was the first to state that water is a compound, though he performed no experiments and probably did not understand the real nature of its constituents. Lavoisier in the same year verified many facts previously noticed but not completely understood, and undoubtedly first clearly recognized and stated what his contemporaries had overlooked. The final proof of the volumetric composition of water was an accurate verification in 1805 by Gay-Lussac and Humboldt of the previous observation that two volumes of hydrogen unite with one volume of oxygen.

**The Gravimetric Composition of Water** is determined by passing dry hydrogen over copper oxide. The method depends upon the fact, previously stated, that many oxides, such as those of lead, copper, and iron, when heated in a current of hydrogen, give up their oxygen, or, chemically speaking, these oxides are reduced to metals. By this reduction the oxygen of the oxide combines with the hydrogen, thereby forming water, which is collected in a weighed tube, while the metal remains behind in the original tube.

A simple form of apparatus for determining the gravimetric composition of water is shown in Figure 12. The cop-

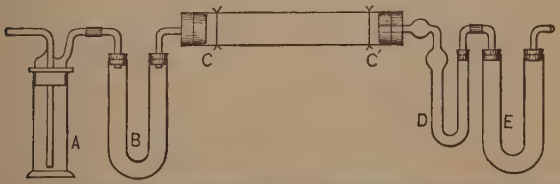



FIG. 12. — Apparatus for determining the gravimetric composition of water.

per oxide is placed in the combustion tube, *CC*, which is made of hard glass. The Marchand tube, *D*, which is filled with calcium chloride, collects and retains the water formed in the combustion tube by the reduction of the copper

oxide. The tubes *A*, *B*, and *E* keep moisture out of the apparatus. The experiment is easily conducted. Copper oxide is placed in the combustion tube, which is then carefully weighed. The Marchand tube, filled with calcium chloride, is also weighed. After the other tubes are properly filled and are connected as shown in the figure, the hydrogen generator is adjusted so that a slow current can be passed through the whole apparatus (from left to right). The combustion tube is now heated, and moisture collects in it; as the heat increases, the copper oxide glows, and the moisture passes into the Marchand tube. When the operation is over and the apparatus is cool and free from hydrogen, the combustion tube and Marchand tube are weighed. The gain in weight of the Marchand tube is the weight of the water formed, while the loss in weight of the combustion tube is the weight of the oxygen removed from the copper oxide and now combined with the hydrogen in the form of water. An example will make this clear. Dumas, who performed this experiment accurately, found substantially that the combustion tube lost 5.251 gm. of oxygen, while the Marchand tube absorbed 5.909 gm. of water. Now the 5.909 gm. of water contains .658 gm. of hydrogen (*i.e.* 5.909—5.251). But .658 and 5.251 are in the same ratio as 1 and 7.98. That is, water contains 1 part of hydrogen and 7.98 parts of oxygen by weight. This ratio is very nearly 1 to 8, and the gravimetric composition of water is often stated as being 1 part hydrogen and 8 parts oxygen. Occasionally the gravimetric composition is stated in per cent, the values being 11.18 per cent hydrogen and 88.82 per cent oxygen. The ratio obtained by Dumas was scarcely questioned until a few years ago. It now appears from an exceptionally accurate determination by Morley that the ratio is 1 to 7.9395. He effected a complete synthesis of water in which the oxygen, hydrogen, and water were weighed. This ratio

is now accepted as the correct one, though the more usual form is 2 to 15.879. The apparatus used by Morley is shown in Figure 13. It was first weighed vacuous (*i.e.* free from air or other gases). The tubes, *aa*, were then connected with the weighed reservoirs of oxygen and hydrogen, and the oxygen was introduced. Sparks were next passed between the platinum wires, *cc*, and the heat ignited the hydrogen, which was slowly admitted, the combination of the gases taking place at *bb*. The water vapor condensed in the tube *dd*, the lower portion of which was immersed in water. The combustion of the hydrogen was continued until a suitable weight of water was formed. The water and its vapor were then converted into ice by putting the apparatus into a freezing mixture; the residual mixture of gases was drawn off and analyzed, passing in its exit through tubes of phosphorus pentoxide in *ee* which retained all traces of water. The whole apparatus was finally weighed, the increase being the weight of the water formed by the combination of known weights of hydrogen and oxygen.

FIG. 13. — Morley's apparatus for determining the gravimetric composition of water.

**Summary.** — Water is a chemical compound of hydrogen and oxygen combined in a fixed ratio by weight, viz. 1 to 7.9395; they are also combined in the ratio of 2.0027 to 1 by volume. Usually these ratios are stated approximately as 2 to 16 by weight and 2 to 1 by volume.

The gravimetric composition of water was first determined about 1820 by Berzelius and Dulong. Their work was verified by Dumas about 1842. The complete synthesis was made in 1895 by Morley.

### Problems

1. What weight (*a*) hydrogen and (*b*) oxygen can be obtained by decomposing 125 gm. of water? 7.486 59.89

2. What volume of (*a*) hydrogen and (*b*) oxygen can be obtained by decomposing 9 l. of water?

3. What weight of hydrogen must unite with 16 gm. of oxygen to form water? What weight with (*a*) 40 gm., (*b*) 70 gm., (*c*) 160 gm.?

4. What volume of oxygen must unite with 2 l. of hydrogen to form water? What volume with (*a*) 40 l., (*b*) 40 cc., (*c*) 40 qt., (*d*) 95 volumes, (*e*) 160 l.?

5. What volume of oxygen is necessary to unite with 100 gm. of hydrogen to form water? (Suggestion: What is the weight of a liter of oxygen?)

6. Hydrogen is passed over 2.48 gm. of hot copper oxide, which at the end of the experiment weighed 2.24 gm.; the water formed weighed .27 gm. In what ratio did the hydrogen and oxygen combine?

7. Berzelius and Dulong, in 1820, obtained the following results in their determinations of the gravimetric composition of water: Loss of weight of copper oxide (in grams), 10.832 and 8.246. Weight of water formed, 12.197 and 9.27. Calculate in each case the ratio in which the hydrogen and oxygen combined. What is the average ratio?

8. Dumas and Stas repeated this experiment about 1842, and found, as an average of nineteen determinations, that 840.161 gm. of oxygen formed 945.439 gm. of water. Calculate the ratio of combination.

9. Morley found that 3.2645 gm. of hydrogen combined with 25.9176 gm. of oxygen. What was the ratio of combination? He found also that 29.1788 gm. of water were produced; what was the experimental error?

## Hydrogen Dioxide

**Hydrogen Dioxide** is a liquid composed of hydrogen and oxygen. But the proportion of the constituents is not the same as in water. It contains approximately two parts of hydrogen and thirty-two parts of oxygen by weight. It is often called hydrogen peroxide, because its relative pro-

portion of oxygen is greater than in water — the other hydrogen oxide.

**Preparation.** — It is prepared by treating barium dioxide (or peroxide) with sulphuric acid. The commercial solution has a variable strength, and usually contains 3 per cent or more of hydrogen dioxide.

**Properties.** — Hydrogen dioxide has a sharp, pungent odor and a bitter, metallic taste. The concentrated solution is a syrupy liquid, but the commercial solution is scarcely distinguishable in appearance from water. It is an unstable compound, which decomposes slowly at the ordinary temperature, and very rapidly if heated. The dilute, commercial solution is somewhat stable, but heat and light decompose it completely into water and oxygen. The ease with which it yields oxygen makes it a good oxidizing agent. Under certain conditions it is also a reducing agent.

**Uses.** — Dilute solutions are used extensively to bleach animal and vegetable matter, such as human hair, ostrich feathers, fur, silk, wool, cotton, bone, and ivory. It is also used as an antiseptic and disinfectant in surgery on account of its oxidizing properties. Large quantities are used to restore the color to faded paintings — a use suggested by Thénard, the discoverer. In the laboratory it is a serviceable reagent.

## CHAPTER VII

**Law, Theory, and Hypothesis — Laws of Definite and Multiple Proportions — Atomic Theory — Atoms and Molecules — Symbols and Formulas — Equations**

**Law and Theory.** — We discover facts by observation and experiment. Phenomena which always occur under the same conditions soon become well-established facts. Our knowledge of the facts which have some relation to each other is often summarized in a brief statement called a **law.** A law is not only an epitome of the uniform behavior of observed facts. It is also a statement which permits us to predict occurrences under like conditions; for if a law is valid for many observed cases, we conclude that it will cover future cases. The essential feature of a law is universal validity.

The ultimate cause of scientific facts is unknown. The explanation we give of facts, especially of groups of related facts, is called a **theory.** Laws are statements about facts; theories are statements of the supposed cause of facts. Laws seldom change, but theories are often modified. Laws are the result of experiment, but theories are the outcome of mental operations. We accept a certain theory until a more satisfactory one is proposed. Sometimes experiment yields results which need further examination or are beyond the realm of our present experimental skill. The temporary explanation or supposition we make in such a case as a guide in further investigation is called an **hypothesis.** An hypothesis is often the forerunner of a theory, and they are not always sharply differentiated.

Laws, theories, and hypotheses are of great service in

chemistry, since they permit us to gather into intelligible statements our knowledge of a vast number of related facts, as well as assist us in discovering new facts and interpreting the phenomena of nature. In this chapter we shall discuss two laws and one theory that are of great importance in chemistry.

**Law of Definite Proportions by Weight.** — When the metal magnesium is heated in the air, it burns with a dazzling flame and yields a grayish powder, due to combination with oxygen. If magnesium is heated so that the product cannot escape, a remarkable relation between their weights is revealed. In order to burn completely 1.52 gm. of magnesium, 1 gm. of oxygen is necessary; and the product, magnesium oxide, weighs 2.52 gm. This product contains, therefore, 60.317 per cent of magnesium and 39.682 per cent of oxygen. Accurate repetitions of this experiment have shown that this proportion by weight is fixed and definite. Again, if a weighed quantity of potassium chlorate is decomposed, 31.903 per cent of potassium, 28.932 per cent of chlorine, and 39.164 per cent of oxygen are always obtained. This means that the proportion of potassium, chlorine, and oxygen which makes up potassium chlorate is fixed and definite. Experiments similar to these show that in all of the chemical compounds which have been examined the different constituents are always present in a definite and unvarying proportion by weight. There are no exceptions to this general fact. This constancy of proportion in chemical compounds is stated as the **Law of Definite Proportions by Weight**, thus: —

*A given chemical compound always contains the same elements in the same proportion by weight.*

This law is one of the fundamental laws of chemistry. It is so confidently believed that if the composition of a com-

pound is found by analysis to vary, chemists conclude that the experimental work is incorrect or that the compound is impure. The law was established as the outcome of a controversy between two French chemists, Proust (1755–1826) and Berthollet (1748–1822). The discussion lasted from 1799 to 1806. Berthollet believed that compounds might have a varying composition. Indeed, by his experiments he detected "gradual changes" in composition. But Proust showed that Berthollet analyzed mixtures and not compounds. (In a mixture the components may be present in any proportion.) Subsequent experiments have only strengthened our confidence in this law.

**Law of Multiple Proportions.** — Proust showed that some elements combine in more than one proportion by weight, and thereby produce two or more distinct compounds. But he failed to notice that if the weight of one element is adopted as constant, the varying weights of the other element or elements are in a simple multiple relation to each other. Dalton discovered this general fact about 1804. The composition of compounds is usually expressed in per cent; but such expressions in a series of compounds reveal nothing about multiple relations. If, however, a constant weight of one constituent is adopted as a basis of comparison, and the composition of the series of compounds is expressed in terms of this weight, then the simple multiple relation which exists between the weights of the other constituent or constituents is clearly seen. Thus, we learn little from the statement that the two compounds of carbon and oxygen contain respectively 27.27 and 42.8571 per cent of carbon and 72.72 and 57.1428 per cent of oxygen. But if in expressing the composition of these compounds we adopt some convenient number, such as 1 for the weight of carbon in each compound, the weights of oxygen will be in the simple integral

ratio of 2 to 1. The five compounds of oxygen and nitrogen, which will soon be studied, aptly illustrate this fact of multiple proportions: —

TABLE TO ILLUSTRATE MULTIPLE PROPORTIONS

| NAME | COMPOSITION IN PER CENT | | ADOPTED WEIGHT | RATIO | |
|---|---|---|---|---|---|
| | Nitrogen | Oxygen | Nitrogen | Nitrogen | Oxygen |
| Nitrous Oxide . . . | 63.636 | 36.363 | 1 | 1 | .57 |
| Nitric Oxide . . . | 46.666 | 53.333 | 1 | 1 | 1.14 |
| Nitrogen Trioxide . | 36.842 | 63.157 | 1 | 1 | 1.71 |
| Nitrogen Peroxide . | 30.434 | 69.565 | 1 | 1 | 2.28 |
| Nitrogen Pentoxide . | 25.925 | 74.074 | 1 | 1 | 2.85 |

From this table it is clear that the weights of oxygen combined with the same weight of nitrogen are as 1 : 2 : 3 : 4 : 5; *i.e.* they are in a relation to each other which can be expressed by small integral numbers. The same simple ratio would be obtained if any other value were substituted for 1, and similar tables may be worked out with other series of compounds.

The general fact of multiple proportions is stated as the **Law of Multiple Proportions**, thus: —

*When two or more elements,* **a**, **b**, **c**, *etc., unite to form a series of compounds, a fixed weight of* **a** *always combines with such weights of* **b** (*as well as of* **c**, *etc.*), *that the ratio between these different weights can be expressed by small* (*usually*), *whole numbers.*

This law, like the law of definite proportions, is a fundamental law. And together with the law of the conservation of matter they have profoundly influenced the theoretical and practical progress of chemistry.

**The Atomic Theory.** — The laws just discussed state in condensed form certain general facts about the quantitative

aspects of chemical change. They point to the existence of chemical units which participate in chemical changes without alteration of weight. But we have no means of detecting or separating these chemical units. Nevertheless, in order to provide a mental picture of this quantitative feature of chemical change a theory has been proposed. It is called the **atomic theory** and was announced in approximately its present form by Dalton, an English chemist, about 1805. According to this theory, (1) chemical elements and compounds consist ultimately of a vast number of very small particles called atoms; (2) chemical change is union, separation, or exchange of undivided atoms; (3) atoms of the same chemical element are alike and have an unvarying weight called the atomic weight; (4) atoms of different elements differ from each other in weight. The atomic theory means in a few words that elements consist of atoms which are endowed with a weight characteristic of each element and which interact chemically in simple proportions.

This theory, it will be observed, deals with the nature of matter and with the quantitative aspects of chemical change. It does not state facts nor does it make facts more valid. It serves merely to assign some explanation, more or less detailed, to facts and laws already formulated. Let us apply the atomic theory to certain facts, *i.e.* restate these facts in terms of the theory. Before proceeding with this application, however, it will be necessary to make a preliminary distinction between an atom and a molecule. About the time of Dalton (1766–1844) the term *particle* was used to include both atom and molecule. But they are not identical. A molecule consists of two or more atoms chemically combined. Accordingly, for the present it will be sufficient to interpret the atom as the smallest part of an element and a molecule as the smallest part of a compound. Thus, the smallest particle of copper which participates in chem-

ical changes is an atom, and the smallest particle of water is a molecule, which consists of hydrogen and oxygen atoms chemically combined. A fuller discussion of atoms will soon be given. But this preliminary distinction will permit us to resume the application of the atomic theory to certain facts. An appreciable mass of the element copper consists of many millions of atoms of copper, all alike — all having the same unvarying weight. Sodium, oxygen, hydrogen, sulphur, carbon, and all the other elements likewise consist of atoms, but the weight of the sodium atom differs from the weight of the atom of copper, carbon, sulphur, and all the other elements. Again, when a chemical change occurs between copper and sulphur, for example, atoms of copper combine with atoms of sulphur and produce molecules of a compound called copper sulphide. Similarly, hydrogen atoms combine with oxygen atoms and produce molecules of water when a spark is passed through a mixture of the two elementary gases. Furthermore, these and all other chemical changes take place not only between vast numbers of atoms, but the quantitative aspects of this multitude of changes conform to the atomic theory. This latter point needs explanation, because it emphasizes the chief feature of the atomic theory, viz. agreement with certain fundamental laws of chemical change. These laws are the law of the conservation of matter, the law of definite proportions, and the law of multiple proportions. According to the atomic theory the weight of an atom is never changed; all other properties may be temporarily lost or buried, but the weight is retained throughout all chemical changes however complex. It is obvious that if atoms never change their weight, the total weight of matter in a chemical change is unvaried, and the law of the conservation of matter follows as a natural consequence. Again, according to the atomic theory when magnesium combines with oxygen, molecules of magnesium oxide are

formed by the union of some whole number of atoms of magnesium with some whole number of atoms of oxygen. Each molecule of magnesium oxide would therefore consist of one or more atoms of magnesium united with one or more atoms of oxygen, and the composition of each molecule of magnesium oxide would be definite; *i.e.* each molecule would contain the same elements united in a definite proportion by weight. In other words, magnesium oxide would always be found to consist of a certain per cent of magnesium and a certain per cent of oxygen. Hence the atomic theory harmonizes with the law of definite proportions. Finally, does the atomic theory conform to the law of multiple proportions? The number of atoms of the combining elements may be the same or different. That is, the ratio of combination may be 1 to 1, 1 to 2, 2 to 3, etc. According to the atomic theory atoms are transferred as wholes; *i.e.* in chemical changes there are no fractions of atoms. Therefore, the proportions of the weights of different elements in a series of compounds must be simple proportions; all multiple relations will be expressible by whole numbers. An illustration will make this point clear. There are two compounds of carbon and oxygen. Analysis shows that in the one containing the less oxygen the ratio of the weight of carbon to oxygen is 3 to 4, and in the other 3 to 8. The second compound contains twice as much oxygen as the first; *i.e.* its molecule contains twice as many atoms of oxygen as a molecule of the first. (Subsequently it will be shown that the first compound is carbon monoxide and contains one atom of oxygen in each molecule, while the second is carbon dioxide and contains two atoms of oxygen in each molecule.) In other words, the weights of oxygen in this series of compounds are in the simple ratio of 1 to 2. The same line of reasoning can be applied to other series of compounds whatever the ratio of combination. Hence the atomic theory harmonizes with the law of multiple proportions.

**Atoms and Molecules.** — It should not be overlooked that the laws of definite and multiple proportions deal with facts. while the atomic theory deals with conceptions which may be true, but which we cannot prove to be true. We often speak of atoms as if they could be perceived by the senses, but we do so simply because such methods of expression help us describe, study, and interpret chemical changes. We also describe elements as if they consisted of free atoms, but atoms do not, as a rule, exist in the uncombined state. As soon as atoms are freed from combination, they at once unite with some other atom or atoms. The particles which make up oxygen gas are not atoms, but a group or chemical combination of atoms. Groups of chemically combined atoms are called molecules. The molecule of an element consists of atoms of one kind only, but the molecule of a compound consists of atoms of two or more different kinds. For example, a molecule of oxygen consists of atoms of the element oxygen, while a molecule of the compound water consists of atoms of oxygen and hydrogen. (A molecule of a few elements contains only one atom.) Atoms are the chemical constituents of molecules. They are the smallest amounts of the elements which are known to participate in chemical changes.

Our views regarding molecules are based on extensive investigation of the properties of gases. The molecule is often spoken of as the physical unit, because in most physical changes molecules are not decomposed. Whereas the atom is called the chemical unit because it is the part of a molecule which as a rule is transferred unchanged in chemical changes. Molecules will be discussed again. (See Chapter XIV.)

Although the atom is conceived to pass as a whole from compound to compound, it should not be inferred that atoms cannot be decomposed under any conditions. The phenomena exhibited by compounds of radium show that

there are particles smaller than atoms. (See Radio-activity.) These very small particles are called corpuscles or electrons. However, the atom is the chemical unit, and whether a single individual or a group of smaller individuals, its weight is not altered in chemical changes.

**Atomic Weights.** — The essential property of matter is weight. According to the atomic theory, different kinds of atoms have different weights. But the absolute weight of an atom cannot be directly determined by any instruments available. We can, however, find the relative weight of an atom; that is, how many times heavier one atom is than another atom. These relative weights are called the **atomic weights** of the elements. If we should adopt 1 as the weight of an atom of hydrogen, the weights of atoms of other elements could be readily expressed in terms of this standard. Thus, the atomic weight of sodium would be 22.88, of oxygen 15.88, of carbon 11.9, etc.; that is, an atom of sodium weighs twenty-three times as much as an atom of hydrogen, etc. For many years hydrogen (= 1) was the standard. But for scientific reasons oxygen is now the standard, and 16 is adopted as its atomic weight instead of 15.88. This change does not alter any facts; it merely changes slightly the numerical values of the atomic weights. Their relation to each other is not changed. The atomic weight of hydrogen becomes 1.008, if oxygen equals 16, and others are proportionally changed. The atomic weights are real weights because they are found by experiment. It should be constantly borne in mind, however, that they are relative weights. That is, the atomic weight of sodium, for example, is 23.00, not 23.00 gm. or any other absolute weight, but 23.00, if the atomic weight of oxygen is 16.

The exact determination of the atomic weight of an element is a difficult operation. Many principles influence the

final selection of the number to be adopted as the atomic weight. This subject is discussed in Chapter XIV. A complete table of the atomic weights is given in the Appendix, § 5. Exact and approximate values of the atomic weights of the important elements can be found in a table on the inside of the back cover, and for most purposes these approximate values can be used, *e.g.* in solving the problems in this and subsequent chapters.

**Chemical Symbols**, which were mentioned in Chapter I, represent single atoms. Thus, H represents one atom of hydrogen, O one atom of oxygen, N one atom of nitrogen. If more than one uncombined atom is to be designated, the proper numeral is placed before the symbol, thus:—

2 H means 2 uncombined atoms of hydrogen,
3 O means 3 uncombined atoms of oxygen,
4 P means 4 uncombined atoms of phosphorus.

But if we wish to represent the atoms as in chemical combination, either with themselves or with other atoms, then a subscript is used instead of a coefficient, thus:—

$H_2$ means 2 atoms of hydrogen in combination,
$N_3$ means 3 atoms of nitrogen in combination,
$P_4$ means 4 atoms of phosphorus in combination.

Symbols not only represent atoms, but they also express atomic weights. Thus, O represents one atom of oxygen, but it also means that this atom weighs 16. Similarly, K represents one atom of potassium, which weighs 39.10.

**Chemical Formulas.**—A formula is a group of symbols which is designed to express the composition of a compound. A given compound, as we have already seen, has a definite composition. In other words, a molecule of a given com-

pound always contains the same number and the same kind of atoms; and since the molecules are alike, the composition of one molecule is the same as the composition of the compound. In writing a formula, the symbols of the different atoms making up a molecule of the compound are placed side by side. Thus $H_2O$ is the formula of water, because one molecule of this compound consists of 2 atoms of hydrogen and 1 atom of oxygen. Similarly, $KClO_3$ is the formula of potassium chlorate. These symbols might be written in a different order, but usage has determined the order in most cases. A formula, as just stated, represents one molecule. Hence, $KClO_3$ represents one molecule of potassium chlorate, and means that the molecule of this compound contains 1 atom each of potassium and chlorine and 3 atoms of oxygen. If we wish to designate several molecules, the proper numeral is placed before the formula, thus : —

2 $KClO_3$ means 2 molecules of potassium chlorate,
3 $H_2O$ means 3 molecules of water,
4 $H_2SO_4$ means 4 molecules of sulphuric acid.

In certain compounds some of the atoms act like a single atom in chemical changes. This fact is often expressed by inclosing the group of atoms in a parenthesis, or by separating it from the rest of the formula by a period. Thus, the formula of ammonium nitrate is $(NH_4)NO_3$, and the formula of alcohol is $C_2H_5.OH$. Water of crystallization is usually indicated in the same manner, $CuSO_4.5\,H_2O$ being the formula of crystallized copper sulphate. The period is sometimes omitted, especially if the composition of the compound is well understood. If a group of atoms is to be multiplied, it is placed within a parenthesis. Thus, the formula of lead nitrate is $Pb(NO_3)_2$. This means that the group $NO_3$ is to be multiplied by 2. That is, lead nitrate might be expressed by $PbN_2O_6$, but for reasons which will be given later the

formula $Pb(NO_3)_2$ is used. The expression $2\ Pb(NO_3)_2$ means that the formula $Pb(NO_3)_2$ is to be multiplied by 2.

Symbols and formulas are sometimes used to represent an indefinite amount of an element or compound. Thus, O is often used to designate oxygen and $H_2SO_4$ sulphuric acid. They are often thus used to label bottles in a laboratory. Such a departure from accuracy should not be allowed to obscure their real meaning.

The complete significance of symbols and formulas can be grasped only by their intelligent use. They should not be committed to memory slavishly. It is desirable, however, to learn the common ones while the substances they represent are being studied, and leave the consideration of their relations until the needed facts have accumulated.

**Molecular Weights.** — Since atoms combine to form molecules, a molecular weight is the sum of the weights of the atoms in the molecule. A molecule of nitric acid contains 1 atom each of hydrogen and nitrogen, and 3 atoms of oxygen; hence its molecular weight is $1 + 14.01 + (16 \times 3) = 63.01$. Given the formula, the molecular weight is easily found by adding the atomic weights. Just as a symbol stands for an atomic weight, so a formula expresses a molecular weight. Molecular weights are real numbers, but they are not found experimentally by merely adding the atomic weights. For convenience we may add the atomic weights, but historically and experimentally molecular weights preceded exact atomic weights. Many facts and principles determine the selection of the molecular weight of a compound. These are discussed in Chapter XIV. For the present, empirical knowledge is sufficient. That is, it will answer all purposes to find the molecular weight of a compound by adding the atomic weights corresponding to the number of atoms in the formula of a molecule of the given compound. By this somewhat arbitrary procedure the molecular weight of water ($H_2O$) is $2 + 16 = 18$; the weight of $2\ H_2O$ is $2(2 + 16) = 36$. Similarly, the molecular weight of lead nitrate ($Pb(NO_3)_2$) is 207.10

$+ 2(14.01 + 48) = 331.12$; the weight of two molecules of lead nitrate ($2\ Pb(NO_3)_2$) is $2 \times 331.12 = 662.24$. Also, the molecular weight of sulphuric acid ($H_2SO_4$) is $(2 \times 1) + 32.07 + (4 \times 16) = 98.07$. Other molecular weights may be calculated in the same way.

It should be noted that the molecular weight of a compound, like the atomic weight of an element, is a relative weight. That is, the molecular weight of water is not 18 gm., but 18, if the atomic weight of oxygen is 16.

**Calculations based on Formulas and Molecular Weights.** — It is evident from the foregoing paragraphs that there is a rigid connection between the molecular weight and the formula of a compound. Since the formula expresses the composition of a compound by means of small integral numbers representing the ratio of the atomic weights in a molecule, it is possible to calculate (1) the composition in per cent, if the formula is known, and (2) the formula, if the composition in per cent is known. Composition in per cent, or, as it is usually designated, **percentage composition**, is readily calculated from the formula of a compound. Let us take a concrete case. The formula of sulphuric acid is $H_2SO_4$. This formula represents a molecular weight of 98, *i.e.* $2 + 32 + 64 = 98$ (using approximate atomic weights). Now if the respective parts of hydrogen, sulphur, and oxygen (viz. 2, 32, 64) are divided by 98 and the quotient then multiplied by 100 (*e.g.* $\frac{2}{98} \times 100$), the product is the per cent of each element in sulphuric acid. It is sometimes more convenient to solve the problem by a proportion. Thus, the proportions for the percentage composition of sulphuric acid are: —

$2 : 98 :: X : 100;\ X = 2.04$ per cent of hydrogen.
$32 : 98 :: X : 100;\ X = 32.65$ per cent of sulphur.
$64 : 98 :: X : 100;\ X = 65.31$ per cent of oxygen.

Total, 100.00 per cent.

By the same method the percentage composition of any compound can be calculated. The **calculation of a formula**, when the atomic weights and the percentage composition are known, is practically the converse of the above process; *i.e.* it is simply the process of finding the small integral numbers which are in the same ratio as the numbers expressing the composition. Suppose we know the composition of sulphuric acid to be hydrogen = 2.04 per cent, sulphur 32.65 per cent, oxygen 65.31 per cent. If the percentage of each element is divided by the corresponding atomic weight, the quotients are 2.04, 1.02, and 4.08. Reducing these quotients to integral numbers (by dividing by 1.02), the final quotients are 2, 1, 4. But these quotients represent the ratio of the atomic weights in a molecule; that is, the relative number of atoms of each element in a molecule. Therefore the formula of sulphuric acid must be $H_2SO_4$. The formula of many compounds can be calculated by this method. (See also Determination of Formulas of Compounds, Chapter XIV.)

**Chemical Equations.** — When substances interact chemically, the definite chemical transformation is called a **reaction.** We have already seen that reactions can be expressed by **equations.** Thus, in Chapter II two of the reactions involved in the preparation of oxygen were expressed as follows: —

Barium Oxide + Oxygen = Barium Dioxide.
Barium Dioxide = Barium Oxide + Oxygen.

It was stated at that point that these equations are crude forms of chemical equations. We can remodel these preliminary equations by using symbols and formulas in place of words, the equations just given then becoming : —

$$BaO + O = BaO_2.$$
$$BaO_2 = BaO + O.$$

The preceding remodeled equations are **ordinary chemical equations**; *i.e.* they are equations showing the kinds and relative weights of the interacting substances.

The scope and interpretation of the ordinary chemical equation can best be set forth by a further discussion of the four kinds of chemical changes.

(1) *Decomposition.* When mercuric oxide is heated, it changes into mercury and oxygen. This reaction is expressed by the equation: —

$$\underset{\text{Mercuric Oxide}}{HgO} = \underset{\text{Mercury}}{Hg} + \underset{\text{Oxygen}}{O}$$

This equation may be read in several ways: (*a*) Mercuric oxide decomposes into mercury and oxygen; (*b*) one molecule of mercuric oxide by decomposition forms one atom of mercury and one atom of oxygen; (*c*) 216 parts by weight of mercuric oxide yield 200 parts by weight of mercury and 16 parts by weight of oxygen (since these are the relative weights found by experiment and reduced to the atomic weight basis); (*d*) mercuric oxide equals mercury plus oxygen.

(2) *Combination.* When magnesium burns in air or in oxygen, magnesium oxide is formed. The equation for the reaction is: —

$$\underset{\text{Magnesium}}{Mg} + \underset{\text{Oxygen}}{O} = \underset{\text{Magnesium Oxide}}{MgO}$$

This equation may be read as follows: (*a*) Magnesium and oxygen combine to form magnesium oxide; (*b*) one atom of magnesium combines with one atom of oxygen and forms one molecule of magnesium oxide; (*c*) 24 parts by weight of magnesium combine with 16 parts by weight of oxygen and yield 40 parts by weight of magnesium oxide; (*d*) magnesium plus oxygen equals magnesium oxide.

(3) *Substitution.* When zinc and sulphuric acid interact, zinc replaces the hydrogen of the sulphuric acid. The equation for this reaction is : —

$$\underset{\text{Zinc}}{Zn} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{H_2SO_4} = \underset{\text{Hydrogen}}{2\,H} + \underset{\substack{\text{Zinc}\\\text{Sulphate}}}{ZnSO_4}$$

This equation may be read as follows : (*a*) Zinc and sulphuric acid interact and form hydrogen and zinc sulphate by the substitution of zinc for the hydrogen of the acid; (*b*) one atom of zinc interacts with one molecule of sulphuric acid and forms two atoms of hydrogen and one molecule of zinc sulphate; (*c*) 65 parts by weight of zinc interact with 98 parts by weight of sulphuric acid and yield 2 parts by weight of hydrogen and 161 parts by weight of zinc sulphate; (*d*) zinc and sulphuric acid equal hydrogen and zinc sulphate.

(4) *Double Decomposition.* When solutions of silver nitrate and sodium chloride are mixed, silver chloride and sodium nitrate are formed. This kind of chemical change is called **double decomposition**, or metathesis, because both of the original compounds undergo decomposition. It is really an exchange or redistribution of atoms; the original compounds undergo decomposition while the final compounds result from a combination of these parts on another plan. Double decomposition may be regarded as the simultaneous occurrence of the other kinds of chemical change, for it involves decomposition, combination, and substitution. However, it is customary to give this kind of chemical change a special name, owing to certain unique features displayed by it. One of these features is the quite frequent formation of an insoluble solid called a **precipitate**. For example, in the reaction just cited the silver chloride is produced as a white, curdy solid, almost insoluble in the final liquid. Double decomposition often results in precipitation. It is

therefore an excellent way to make tests, and it finds numerous applications in chemical analysis. The equation for the foregoing reaction is : —

$$\underset{\text{Silver Nitrate}}{AgNO_3} + \underset{\text{Sodium Chloride}}{NaCl} = \underset{\text{Silver Chloride}}{AgCl} + \underset{\text{Sodium Nitrate}}{NaNO_3}$$

This equation may be read as follows: (*a*) Silver nitrate and sodium chloride interact and form silver chloride and sodium nitrate by double decomposition; (*b*) one molecule of silver nitrate interacts with one molecule of sodium chloride and forms one molecule of silver chloride and one molecule of sodium nitrate; (*c*) 170 parts by weight of silver nitrate interact with 58.5 parts by weight of sodium chloride and yield 143.5 parts by weight of silver chloride and 85 parts by weight of sodium nitrate; (*d*) silver nitrate plus sodium chloride equals silver chloride plus sodium nitrate.

In the foregoing discussion of the four kinds of chemical change similar statements are designated by the same letter. Let us consider each lettered group. Under (*a*) in each case nothing is said about the physical conditions attending the chemical change recorded by the equation, because such accompaniments are outside the scope of ordinary chemical equations. Thus, in the equations $HgO = Hg + O$ and $Mg + O = MgO$ there is no hint whatever that the mercuric oxide must be kept at a high temperature or that the magnesium unites vigorously with oxygen at a relatively low temperature. Again, in the equations $Zn + H_2SO_4 = 2\ H + ZnSO_4$ and $AgNO_3 + NaCl = AgCl + NaNO_3$ there is no suggestion that the sulphuric acid, sodium chloride, and silver nitrate must be dissolved in water, nor that the zinc sulphate which is produced remains in solution while the silver chloride is precipitated. Furthermore, heat is often liberated in chemical changes, *e.g.* by the interaction of zinc and hydrochloric acid; but in the ordinary chemical equation as given

above this fact is ignored. Hence we conclude (1) that ordinary chemical equations tell nothing about the physical conditions (*i.e.* temperature, physical state, solution, etc.) under which the chemical reaction starts, proceeds, and ends. Again, in (*b*) and (*c*) the chemical equations are made up of the smallest integral number of atoms and molecules involved in the chemical change. The equation is a sample, so to speak, of the vast number of like changes which we call the chemical change. What determines the number of atoms and molecules to be incorporated in an equation? The answer to this question necessitates the discussion of several topics. First, equations are the outcome of experiments. They follow experiments, and are designed to be compact, symbolic expressions of certain phases of a particular chemical change. They tell at a glance one part of a complex story. Second, ordinary chemical equations express quantitative relations. That is, they not only emphasize the fact that a chemical change exemplifies the law of the conservation of matter, but they also show the proportions of the participating substances. For example, experiment shows that when a given weight of mercuric oxide is decomposed into mercury and oxygen, the actual weights involved are in the ratio of 216 to 200 to 16 respectively. Corresponding values are found for each equation. These values, which differ of course with different equations, are real and must be known before the particular equation can be written correctly. In fact, they precede every equation, although we often overlook this fact in using equations. Third, before a chemical equation can be written certain facts must be known. One of these is the composition of each compound involved; *i.e.* not merely the per cent of each constituent in each compound, but the proportion of each constituent in terms of the atomic weights of the elements. In other words, before an equation can be written it is

necessary to know the symbol and atomic weight of each element and the formula and molecular weight of each compound. These, as previously stated, may be found for the present by utilizing the table of atomic weights given in the Appendix, § 5, supplemented by information given in the text. It is also essential to know the proportions in which the original substances (often called factors) interact and in which the final substances (sometimes called products) are produced.

We draw as a second conclusion from this rather long discussion of the statements recorded above (in (*b*) and (*c*)) that (2) an ordinary chemical equation shows by means of the appropriate number of atoms and molecules not only the kind but the relative quantities of substances before and after a chemical change.

(*d*) The verbal interpretation of an ordinary chemical equation is very often compressed into a form which simulates the algebraic equation. But ordinary chemical equations cannot be subjected to transposition or factoring. In a certain sense, therefore, it is anomalous to say that mercuric oxide *equals* mercury *plus* oxygen. There will be little or no difficulty, however, if it is understood that the ordinary chemical equation is not an algebraic expression which attempts to describe a chemical change in all its aspects. Objections have been raised to the use of the sign of equality (=), and an arrow is sometimes substituted for it, the equation then becoming, for example, $HgO \rightarrow Hg + O$. Many equations are used merely to express the gravimetric proportions in which chemical reactions take place; in such equations we shall use the sign of equality. Doubtless certain facts can best be expressed by equations in which the sign of equality is replaced by an arrow. The special style or form of an equation depends upon the part of the chemical story it is designed to epitomize. Later we shall have occasion to use

other forms of equations. (See ionic, thermal, and gas equations, and equilibrium.)

We draw finally a third and comprehensive conclusion; viz. (3) ordinary chemical equations are expressions showing by symbols and formulas the quantitative relations between all the substances involved in chemical reactions. Each equation is the outcome of experiment, and although the equation contains the signs used in algebraic equations, it has none of the properties of an algebraic equation except equality between the total weights on each side of the equation; the chemical equation, furthermore, is limited to a statement of the chemical distribution of atoms and does not reveal any facts about the physical phenomena which invariably accompany chemical changes.

**Making Equations.** — It is clear that the task of making a correct chemical equation is not easy. Several avenues are open to the beginner. The short equations can be committed to memory or worked out by methods soon to be outlined; the long ones can be interpreted by the facts recorded in connection with the experiment and then referred to later, as occasion demands. The student must not forget that each chemical reaction has its own equation and that similarity of names and of chemical changes does not imply uniformity of equations. A word of caution must also be uttered against attempts to write an equation by mere guess work and then expect the facts to coincide with this pseudo-equation.

One **method of working out simple chemical equations** will be clear from the following cases: (*a*) When magnesium is heated in oxygen (or in air), the ratio by weight in which the two elements combine is 3 : 2. This result is expressed in terms of the atomic weights of the elements involved. Let $y$ equal the number of atomic weights of magnesium

and $z$ the number of atomic weights of oxygen. Then we can write a preliminary equation thus: —

$y \times$ at. wt. of magnesium : $z \times$ at. wt. of oxygen = 3 : 2.

The atomic weight of magnesium is found by the table on the back cover to be 24 and that of oxygen to be 16. Substituting these values, we have the equation : —

$$y \times 24 : z \times 16 = 3 : 2$$

By inspection $y = z$, and the simplest value of each is 1. Now the symbol Mg expresses 24 parts of magnesium and the symbol O expresses 16 parts of oxygen. Therefore Mg and O are the symbols representing the smallest number of atoms equivalent arithmetically to the ratio (3 : 2) found by experiment. The formula of the product formed by their combination is therefore MgO, and the simplest equation expressing the chemical change is —

| Mg | + | O | = | MgO |
|---|---|---|---|---|
| Magnesium | | Oxygen | | Magnesium Oxide |

(*b*) Again, suppose we wish to find the simplest equation for the reaction between hydrogen and oxygen in the formation of water. Experiment shows that hydrogen and oxygen combine in the ratio 1 : 8 by weight. Pursuing the same line of argument as above, let $y =$ the number of atomic weights of hydrogen, and $z$ that of oxygen. The preliminary equation is : —

$y \times$ at. wt. of hydrogen : $z \times$ at. wt. of oxygen = 1 : 8

The atomic weight of hydrogen is 1 and of oxygen is 16. The equation now becomes —

$$y \times 1 : z \times 16 = 1 : 8$$

By inspection, $y = 2z$, and the simplest values are $y = 2$ and $z = 1$. Now the symbol H stands for 1 part of hydrogen,

and O for 16 parts of oxygen. Therefore, 2 H and O are the symbols representing the smallest number of atoms equivalent arithmetically to the ratio (1 : 8) found by experiment. The formula of the product of their combination is $H_2O$, and the simplest equation is —

$$2\,H + O = H_2O$$

All equations are not equally simple, but by a similar argument based upon the facts found by experiment many simple equations may be developed.

**Another method** is often possible. When we know the factors and products of a reaction, we can find their symbols or formulas in the book, construct a preliminary equation, and then balance the equation; *i.e.* select the proper coefficients, subscripts, or both, so that there shall be an equal number of atoms of each element on both sides of the equation. An example will make this method clear. When phosphorus burns in oxygen, phosphorus pentoxide is formed. The preliminary equation is —

$$P + O = P_2O_5$$

Here it is evident that to balance the equation we need 2 P and 5 O on the left. Hence the final equation is —

$$2\,P + 5\,O = P_2O_5$$

Again, when zinc and hydrochloric acid interact, hydrogen and zinc chloride are formed. The preliminary equation made from the symbols and formulas is —

$$Zn + HCl = H + ZnCl_2$$

By inspection, it is evident that two atoms of chlorine are on the right and only one on the left. To obtain $Cl_2$ it is necessary to write 2 HCl. But 2 HCl means not only 2 Cl but 2 H. Hence the equation becomes —

$$Zn + 2\,HCl = 2\,H + ZnCl_2$$

A final inspection shows that an equal number of atoms of each element is on both sides of the equation.

Many equations may be written by applying these methods to the facts found by experiment (see exercises at the end of this chapter).

**Equations for Preceding Reactions.** — The equations corresponding to many reactions already discussed may appropriately be collected here, partly for their retrospective value and partly for future use. The equation for the preparation of oxygen from mercuric oxide is —

$$\underset{\text{Mercuric Oxide}}{HgO} = \underset{\text{Mercury}}{Hg} + \underset{\text{Oxygen}}{O}$$

When sulphur, carbon, magnesium, and iron are burned in air (or in oxygen), the equations are —

$$\underset{\text{Sulphur}}{S} + \underset{\text{Oxygen}}{2O} = \underset{\text{Sulphur Dioxide}}{SO_2}$$

$$\underset{\text{Carbon}}{C} + \underset{\text{Oxygen}}{2O} = \underset{\text{Carbon Dioxide}}{CO_2}$$

$$\underset{\text{Magnesium}}{Mg} + \underset{\text{Oxygen}}{O} = \underset{\text{Magnesium Oxide}}{MgO}$$

$$\underset{\text{Iron}}{3Fe} + \underset{\text{Oxygen}}{4O} = \underset{\text{Magnetic Iron Oxide}}{Fe_3O_4}$$

The equation for the preparation of hydrogen from zinc and hydrochloric acid is —

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Hydrochloric Acid}}{2HCl} = \underset{\text{Hydrogen}}{2H} + \underset{\text{Zinc Chloride}}{ZnCl_2}$$

When hydrogen burns or when a mixture of hydrogen and oxygen is exploded, the equation is —

$$\underset{\text{Hydrogen}}{2H} + \underset{\text{Oxygen}}{O} = \underset{\text{Water}}{H_2O}$$

The equation for the reaction in determining the gravimetric composition of water is —

$$\underset{\substack{\text{Copper}\\\text{Oxide}}}{CuO} + \underset{\text{Hydrogen}}{2H} = \underset{\text{Water}}{H_2O} + \underset{\text{Copper}}{Cu}$$

The equation for the decomposition of potassium chlorate is —

$$\underset{\substack{\text{Potassium}\\\text{Chlorate}}}{KClO_3} = \underset{\substack{\text{Potassium}\\\text{Chloride}}}{KCl} + \underset{\text{Oxygen}}{3O}$$

The interaction of sodium and water is represented thus: —

$$\underset{\text{Sodium}}{Na} + \underset{\text{Water}}{H_2O} = \underset{\text{Hydrogen}}{H} + \underset{\substack{\text{Sodium}\\\text{Hydroxide}}}{NaOH}$$

When phosphorus burns in air (or oxygen), the equation is —

$$\underset{\text{Phosphorus}}{2P} + \underset{\text{Oxygen}}{5O} = \underset{\substack{\text{Phosphorus}\\\text{Pentoxide}}}{P_2O_5}$$

**Calculations based on Equations.** — Since equations are expressions of the relative quantities of the substances involved in chemical reactions, it is possible to solve many arithmetical problems arising from reactions. An equation states the proportions which participate chemically in a reaction. Obviously, any convenient weights of zinc and sulphuric acid might be brought together, but the proportions according to which the factors react and the products are formed are always expressed by the equation —

$$\underset{\text{Zinc}}{Zn} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{H_2SO_4} = \underset{\text{Hydrogen}}{2H} + \underset{\substack{\text{Zinc}\\\text{Sulphate}}}{ZnSO_4}$$

| 65 | 98 | 2 | 161 |
|---|---|---|---|

If zinc and sulphuric acid are brought together in any other proportion, a part of one or the other will be left over unused.

The equation above means that zinc and sulphuric acid always interact in the proportion of 65 and 98, and produce hydrogen and zinc sulphate in the proportion of 2 and 161. We may read grams, ounces, kilograms, or any other unit in connection with these numbers, but the same unit must be used throughout the calculations. Therefore, if we know the actual weight of one substance participating in a reaction, all other weights involved can be readily calculated. Suppose 45 gm. of zinc interact with sulphuric acid; the weights of (*a*) acid required, (*b*) hydrogen formed, and (*c*) zinc sulphate produced are calculated as follows: —

(1) Write the chemical equation for the reaction, thus: —

$$Zn + H_2SO_4 = 2\,H + ZnSO_4$$

(2) Place under each term of the equation its atomic or molecular weight,[1] as the case may be, thus: —

$$\underset{65}{Zn} + \underset{98}{H_2SO_4} = 2\,\underset{2}{H} + \underset{161}{ZnSO_4}$$

(3) Place above the proper terms the known weight and required weight (*i.e.* X, Y, Z, etc.) involved in the problem, thus: —

$$\overset{45}{\underset{65}{Zn}} + \overset{X}{\underset{98}{H_2SO_4}} = 2\,\overset{Y}{\underset{2}{H}} + \overset{Z}{\underset{161}{ZnSO_4}}$$

(4) State in the form of a proportion the four terms involved, remembering that the known and required weights are in the same ratio as the atomic and molecular weights. Thus, the three proportions in the given problem are: —

(*a*) 45 : X : : 65 : 98; X = 67.8 gm. sulphuric acid.
(*b*) 45 : Y : : 65 : 2; Y = 1.38 gm. hydrogen.
(*c*) 45 : Z : : 65 : 161; Z = 111.4 gm. zinc sulphate.

Similar problems can be solved by this method.

[1] The atomic weights are given in the table on the inside of the back cover. Molecular weights are obtained by adding the proper atomic weights.

### Problems and Exercises

1. Calculate the percentage composition of (*a*) water ($H_2O$), (*b*) zinc sulphide (ZnS), (*c*) zinc carbonate ($ZnCO_3$), (*d*) potassium chlorate ($KClO_3$).

2. Calculate the percentage composition of (*a*) sugar ($C_{12}H_{22}O_{11}$), (*b*) calcium sulphate ($CaSO_4$), (*c*) zinc sulphate ($ZnSO_4$), (*d*) magnesium oxide (MgO), (*e*) copper oxide (CuO).

3. Calculate the molecular weight of the following compounds by finding the sum of the atomic weights: (*a*) copper sulphate ($CuSO_4$), (*b*) barium chloride ($BaCl_2$), (*c*) manganese dioxide, (*d*) calcium oxide, (*e*) sodium hydroxide, (*f*) potassium hydroxide, (*g*) sodium carbonate ($Na_2CO_3$), (*h*) potassium nitrate ($KNO_3$).

4. Calculate the formula of the compounds which have the indicated composition, and give the name of each compound: (*a*) H = 11.18, O = 88.82; (*b*) Na = 32.39, O = 45.07, S = 22.54; (*c*) C = 27.27, O = 72.72.

5. Calculate the formula of the compounds which have the following composition: (*a*) N = 82.353, H = 17.647; (*b*) O = 30, Fe = 70; (*c*) H = 1, C = 11.99, O = 47.95, K = 39.06.

6. How much oxygen can be prepared from (*a*) 122.5 gm. of potassium chlorate, (*b*) 245 gm., and (*c*) 421 gm.?

7. (*a*) How much oxygen can be prepared from 50 gm. of potassium chlorate, and (*b*) how much potassium chloride will remain?

*Ans.* (*a*) = 19.59, (*b*) = 30.41.

8. A certain weight of potassium chlorate was heated until completely decomposed. The residue weighed 20.246 gm. (*a*) What was its weight? (*b*) How much oxygen was evolved?

*Ans.* (*a*) = 33.29, (*b*) = 13.044.

9. What weight of potassium chlorate is needed to generate 144 gm. of oxygen? *Ans.* 367.5.

10. What weight of potassium chloride remains after obtaining 8 gm. of oxygen from potassium chlorate? *Ans.* 12.416.

11. How many grams of oxygen can be generated from 490 gm. of potassium chlorate? *Ans.* 192.

12. How much hydrogen can be prepared from (*a*) 65 gm. of zinc, (*b*) 130 gm., (*c*) 297 gm.? *Ans.* (*c*) 9.14.

13. How much zinc is needed to prepare (*a*) 2 gm. of hydrogen, (*b*) 14 gm., and (*c*) 17 gm.?

14. How much zinc sulphate can be prepared from (*a*) 98 gm. of sulphuric acid, (*b*) 196 gm., (*c*) 427 gm.? *Ans.* (*c*) 701.5.

15. A balloon holds 132.74 kg. of hydrogen. How much (*a*) zinc and (*b*) sulphuric acid are needed to produce the gas?

*Ans.* (*a*) 4314.05, (*b*) 6504.26.

16. How much (*a*) mercury and (*b*) oxygen can be obtained from 10 gm. of mercuric oxide? (Equation is $HgO = Hg + O$, or $216 = 200 + 16$.) *Ans.* (*a*) 9.259, (*b*) .74.

17. How much mercury will remain after obtaining 48 gm. of oxygen by heating mercuric oxide?

18. A lump of carbon weighing 24 gm. is burned in air. What weight of (*a*) carbon dioxide is formed and (*b*) oxygen is needed? (*c*) If a liter of oxygen weighs 1.43 gm., what volume of oxygen is needed? (Equation is $C + 2O = CO_2$, or $12 + 32 = 44$.)

*Ans.* (*c*) 44.75 l.

19. What weight of carbon dioxide is formed by burning 112 lb. of coal containing 15 per cent of impurities?

20. A lump of sulphur weighing 32 gm. is burned in air. Calculate the weight of (*a*) oxygen needed and (*b*) sulphur dioxide formed. (Equation is $S + 2O = SO_2$, or $32 + 32 = 64$.)

21. Calculate the weight of oxygen needed to burn 731 gm. of sulphur containing 15 per cent of impurities. *Ans.* 621.35.

22. What weight of sulphur dioxide is formed by burning 67 per cent of 8794 kg. of sulphur?

23. Write the equations for the combination of sulphur and oxygen when they unite in the ratio (*a*) 1 : 1 and (*b*) 2 : 3. So also for carbon and oxygen in the ratio (*a*) 3 : 8 and (*b*) 3 : 4. Similarly for nitrogen and hydrogen in the ratio 4.66 : 1.

24. State how the following equation illustrates decomposition, combination, and substitution: —

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2\,HCl.$$

25. Write equations for the following reactions: (*a*) Magnesium and hydrochloric acid form magnesium chloride and hydrogen. (*b*) Sodium sulphate and barium chloride form barium sulphate and sodium chloride. (*c*) Calcium carbonate and hydrochloric acid form calcium chloride, water, and carbon dioxide. (*d*) Lime (see index) and carbon dioxide form calcium carbonate. (*e*) Chlorine and phosphorus form phosphorus trichloride. (*f*) Carbon and copper oxide (CuO) form copper and carbon dioxide.

Outline on Chemical Equations.

# CHAPTER VIII

## The Atmosphere — Argon and Related Elements — Nitrogen

THE atmosphere is the great envelope of gas surrounding the earth. It extends into space to an estimated height of fifty to two hundred miles. We live at the bottom of this vast ocean of air, as it is often called.

Aristotle (384–322 B.C.) regarded air as one of the four elementary principles whose combinations made up all substances in the universe. The other three were earth, fire, and water. He taught that air possesses two fundamental properties — heat and dampness. The early chemists used the word *air* in the sense in which the word *gas* is now employed. Thus, we have already learned that hydrogen was first called inflammable air.

The terms *atmosphere* and *air* are often used interchangeably, though by air we usually mean a limited portion of the atmosphere. Many skillful chemists have studied the action of air on living things, its relation to combustion, the effect of its weight, its composition, and its varied properties. Their work has contributed many fundamental facts to science.

**General Properties of the Atmosphere.** — Air has weight. We often use the expression "light as air." But a cubic foot of air weighs 1.28 oz. and a room $40 \times 50 \times 25$ ft. contains about two tons of air. A liter of dry, normal air at 0° C. and 760 mm. weighs 1.293 gm. The total weight of the atmosphere has been estimated to be five thousand millions of millions of tons. The enormous mass resting upon the earth exerts a pressure which is about fifteen pounds on every square inch. The amount of pressure upon a

square inch is called "an atmosphere," and it is sometimes used as a unit of pressure; *e.g.* three atmospheres means a pressure of forty-five pounds per square inch. It is atmospheric pressure which causes water to rise in pumps and flow through siphons. Atmospheric pressure is exerted in all directions and is variable. It is measured by the barometer. The normal or standard pressure of the atmosphere, as already stated, is equal to the pressure of a column of mercury which is 760 mm. (or 29.92 in.) high. In very accurate experiments certain mathematical corrections must be made in the height of the column as read on the barometer scale, but in ordinary work it is necessary to know the height only of the mercury column in order to know the pressure. The pressure of the atmosphere varies as the height and composition of the atmosphere vary, and the barometer changes accordingly.

**Ingredients of the Atmosphere.** — The atmosphere is a mixture of several gases. But since this mixture always contains approximately 78 parts of nitrogen and 21 parts of oxygen by volume, we often speak of air as consisting solely of these two gases. Besides this large proportion of oxygen and nitrogen, the air always contains small and variable proportions of water vapor and carbon dioxide gas. In addition to these four ingredients, air always contains the gas argon (and the related inert gases), and usually very small proportions of ozone, hydrogen, hydrogen dioxide, compounds related to ammonia and nitric acid, dust, and germs. The composition varies but slightly in different localities. Near the city air may contain a relatively larger proportion of dust, ammonia, sulphur compounds, and acids; in the country the proportion of ozone is relatively large; over the ocean and near the seacoast the air contains salt.

**General Properties of Nitrogen.** — The chemical element, nitrogen, which constitutes about 78 per cent of the atmosphere (by volume), is a colorless gas, and has no taste or odor. It is somewhat lighter than air, and is slightly soluble in water. In many respects it differs markedly from oxygen. Thus, it will not support combustion, neither will it burn, nor sustain life. Animals die if left in nitrogen. Nitrogen is not poisonous, for the air we breathe contains a large proportion of nitrogen. Its function in the atmosphere is to dilute the oxygen. It is an inert element compared with many others; *i.e.* it combines directly with only a few other elements, and many of its compounds easily decompose; at the ordinary temperature it is chemically indifferent.

The fact that a candle flame quickly goes out and a mouse soon dies in nitrogen was first observed by Rutherford, a Scottish physician, who discovered the gas in 1772. Soon after, Lavoisier showed the true relation of nitrogen to the atmosphere. To emphasize the inability of the gas to support life, he called the new gas *azote*, the name now used for it by French chemists.

**Oxygen and Nitrogen in the Atmosphere.** — The chemical activity of the atmosphere is due to the free oxygen it contains, as we have already learned in studying oxygen. If the air were largely oxygen, rusting and decay would proceed with astonishing rapidity, and fires once started would burn with great violence. On the other hand, nitrogen is chemically inactive, and if the air contained much more than the normal amount, the chemical action of oxygen would be slower. Oxygen alone is too active, while nitrogen alone is rather inactive. To be serviceable to man, oxygen must be diluted with nitrogen, while nitrogen must be accompanied by a small proportion of oxygen.

The presence of oxygen and nitrogen in the atmosphere and the functions of the two gases were first clearly explained by Lavoisier

in 1777, though many others — Boyle, Priestley, Rutherford, and Scheele — helped solve the problem.

**Composition of the Atmosphere.** — Samples of air from various parts of the globe show a remarkable uniformity of composition. For many years it was believed that pure air consisted solely of oxygen and nitrogen. But in 1895 it was found that nearly 2 per cent (by weight) of the gas hitherto called nitrogen is argon. (See Argon, below.) According to the most recent results, the following is —

THE COMPOSITION OF PURE NORMAL DRY AIR

| INGREDIENT | PERCENTAGE | |
|---|---|---|
| | By Volume | By Weight |
| Nitrogen . . . . . | 78.122 | 75.539 |
| Oxygen . . . . . | 20.941 | 23.024 |
| Argon . . . . . | 0.937 | 1.437 |

The composition of the atmosphere was studied by Priestley, but his results were conflicting. Cavendish, in 1781, was the first to show that the proportion of oxygen and nitrogen in air is nearly constant. Since his time this result has been confirmed by many chemists, especially by Bunsen. In recent years the composition of the atmosphere and the properties of its inert components have been assiduously studied by Ramsay and others.

**The Volumetric Composition of Air** can be found in the laboratory by introducing a known volume of pure air into a eudiometer and exploding it with a known and sufficient volume of hydrogen. The nitrogen does not participate in the chemical change, but all the oxygen in the air combines with twice its volume of hydrogen, forming a minute quantity of water; hence one third of the diminution in volume is the volume of oxygen in the air. The difference between

the volume of oxygen found and the original volume of air is the volume of the other constituents — chiefly nitrogen. An illustration will make this experiment clear. Suppose (1) we mix and explode 100 cc. of air and 50 cc. of hydrogen, or 150 cc. in all, and (2) the residue measures 87 cc. Now, $150 - 87 = 63$, hence 63 cc. of the total volume of the mixture combined to form water (the 63 consisting of all the oxygen and part of the hydrogen). But one third of the 63 cc. is the oxygen which was in the original volume of air, because oxygen and hydrogen unite volumetrically in the ratio of 1 to 2. Hence, $63 \div 3 = 21$, the volume of oxygen in 100 cc. of air. The remainder, 79 cc., is nitrogen, argon, and other gases.

**Another Method**, often used to determine the volumetric composition of the air, is based on the fact that phosphorus combines slowly with oxygen, even at the ordinary temperature. The operation is performed by inserting a piece of phosphorus (attached to a wire) into a graduated glass tube containing a measured volume of air. White fumes indicate immediate action. These fumes are solid particles of phosphorus pentoxide. They soon dissolve in the water, which rises higher in the tube, as the oxygen combines with the phosphorus. In a few hours the phosphorus is removed, and the volume of gas is read. The difference between the first and last volumes is oxygen. The gas remaining in the tube is a mixture of nitrogen and argon. In performing this experiment unusual care must be taken not to touch the phosphorus with dry hands.

In both of the methods described above all gas volumes are of course reduced to standard conditions and the dry state.

**The Gravimetric Composition of Air** was first accurately determined in 1841 by the French chemists Dumas and Boussingault. The average result of many experiments was: —

| | |
|---|---|
| Nitrogen . . . . . | 77 parts by weight, |
| Oxygen . . . . . | 23 parts by weight. |

We know now, however, that the correct proportions are —

| | | |
|---|---|---|
| Oxygen . . . . . | 23.024 | parts by weight, |
| Nitrogen . . . . . | 75.539 | parts by weight, |
| Argon . . . . . | 1.437 | parts by weight. |

In making the gravimetric determination, they passed pure air through a weighed tube containing copper, and arranged so that heat could be applied. The oxygen of the air combined with the copper, while the nitrogen passed on into a weighed globe. Both tube and globe increased in weight. The increase in the tube was the weight of the oxygen, while the increase in the globe was the weight of the nitrogen.

**Water Vapor in the Atmosphere.** — Water vapor is always present in the atmosphere, owing to constant evaporation from the ocean, other bodies of water, and the soil. The total amount is large, though variable. A given volume of air at a given temperature will absorb a definite volume of water vapor and no more. The amount absorbed depends largely upon the temperature. Air containing its maximum amount of water vapor at a given temperature is said to be saturated at that temperature, or to contain 100 per cent of water vapor. The saturation point is also called the **dew-point**. On a pleasant day, the relative humidity, *i.e.* the relative amount of water vapor present, may vary from 30 to 90 per cent, the average being about 50 per cent, though it varies with the locality. Warm air holds more vapor than cool air. The amount of water vapor in the air has a marked influence on the physical condition of man. The depressing weather during " dog days " is due to the high relative humidity of the air, which sometimes reaches nearly 100 per cent. The specialized forms of life, both animal and vegetable, found in deserts are largely due to the dry air. The languor felt in a " close " room or crowded hall is partly caused by the excess of water vapor in the " bad " air. The presence of water vapor in the air is shown

by the moisture which collects on the outside of a vessel containing cold water, such as a pitcher of iced water. The moisture comes from the air around the vessel. For a similar reason, water pipes in a cellar and the cellar walls themselves are moist in summer. The deliquescence of calcium chloride, common salt, and other substances likewise reveals the presence of water vapor in the air. (See Deliquescence.) When the temperature of the air falls sufficiently, the water vapor condenses and is deposited in the form of dew, rain, fog, mist, frost, snow, sleet, or hail. The clouds are masses of water vapor which has been condensed by the cold of the upper air.

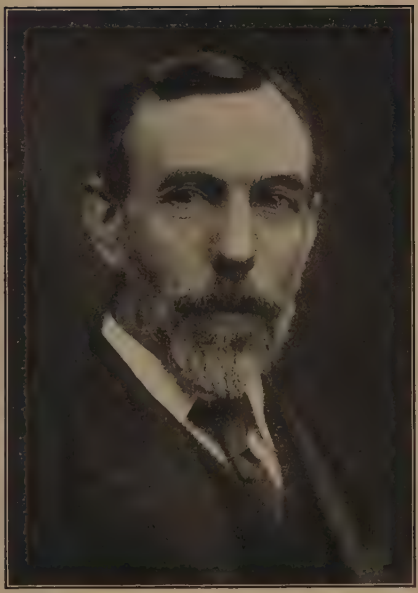
**Carbon Dioxide in the Atmosphere.** — Carbon dioxide is one product of the respiration of animals and of the combustion and decay of organic substances. By these processes an immense quantity of carbon dioxide is being constantly poured into the atmosphere. The proportion in the atmosphere is variable, though not between such wide limits as the water vapor. The proportion in normal air is 3 to 4 parts in 10,000 parts of air. Over the ocean the proportion is smaller, but in the air of cities it is greater. In crowded rooms the proportion is often as high as 33 parts in 10,000. The proportion of carbon dioxide in the atmosphere as a whole is practically constant, largely owing to the fact that this gas is an essential food of plants. (See Carbon Dioxide.) The presence of carbon dioxide in the air is detected by calcium hydroxide. If a solution of calcium hydroxide is exposed to the air, the carbon dioxide interacts with the calcium hydroxide, forming a thin, white crust of insoluble calcium carbonate on the surface of the liquid. If air is drawn through calcium hydroxide, the liquid becomes milky, because the fine particles of calcium carbonate remain temporarily suspended in the liquid. The

purity of air is often determined by finding out what proportion of carbon dioxide it contains. If a known volume of dry air is drawn through a known weight of calcium hydroxide or similar liquid, the increase in weight will be the weight of carbon dioxide in the volume of air used. The equation for the interaction of carbon dioxide and calcium hydroxide is : —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Calcium Hydroxide}}{Ca(OH)_2} = \underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

The different gases in the atmosphere are not arranged in layers according to their densities. They are in constant circulation. (See Diffusion.) Hence carbon dioxide, though heavier than oxygen and nitrogen (volume for volume), does not remain nearest the ground, but is distributed through the air. In a few exceptional localities, carbon dioxide arises from volcanic openings faster than it can diffuse, and fills the cave or adjacent valley.

**Argon (A) and Related Elements.** — Argon, as already stated, is an essential and constant component of the atmosphere. Argon was discovered in 1895 by Rayleigh and Ramsay. Rayleigh found that nitrogen extracted from air had a greater weight than an equal volume of nitrogen obtained from compounds of nitrogen. Consequently, they believed that the nitrogen from air contained another gas hitherto overlooked. A series of elaborate experiments showed that after the oxygen and nitrogen were removed from purified air, there still remained a small quantity of a new gas, which they called argon. It may be obtained (1) by passing pure air over heated copper to remove the oxygen, and then the remaining gas over heated magnesium or calcium to remove the nitrogen; or (2) by passing electric sparks through a mixture of air and oxygen, and removing



SIR WILLIAM RAMSAY

the compound of oxygen and nitrogen as fast as it is formed. The latter method is a repetition of the one used by Cavendish when he determined the composition of air, and he would have no doubt discovered argon had he continued his investigations. As stated above, the proportion in the atmosphere is .937 per cent by volume and 1.437 per cent by weight.

Argon is a colorless, odorless gas. It dissolves in water to the extent of about 4 volumes in 100. It has been liquefied and solidified; the boiling point of liquid argon is — 186° C. and the melting point of the solid (which is colorless) is — 189.5° C. A conspicuous property of argon is its lack of chemical activity. No compounds of this element have as yet been prepared or discovered. The name *argon* is happily chosen, being derived from Greek words signifying inert.

Helium (He), neon (Ne), krypton (Kr), and xenon (Xe) are inert gases discovered by Ramsay subsequently to argon. They constitute an exceedingly minute proportion of the atmosphere. Like argon they do not appear to form compounds. Their proportions in the atmosphere are estimated by Ramsay as follows :—

Helium, 1 to 2 parts per million,
Neon, 1 to 2 parts per hundred thousand,
Krypton, 1 part in 20,000,000,
Xenon, 1 part in 170,000,000.

Helium was detected in the atmosphere of the sun by Lockyer in 1868. It was found by Ramsay, soon after he discovered argon, in the gases expelled from certain minerals and in the gas and water of certain mineral springs. Recently it has become conspicuous as one of the disintegration products of radium. (See Radio-activity.)

The process of separating the inert gases of the atmosphere from each other is an excellent illustration of modern ex-

perimental methods. The mixture of the five gases is compressed in a bulb and cooled to about — 185° C. by immersion in liquid air; the argon, krypton, and xenon condense to a liquid in which the helium and neon dissolve. When the bulb is removed and warmed, the helium and neon together with considerable argon escape first into a special bulb, the argon next, and finally the krypton and xenon. Several repetitions, however, are necessary to separate the argon from the helium and neon and the krypton and xenon, as well as the last two from one another. By immersing the bulb containing the helium and neon in liquid hydrogen, the neon solidifies and the helium can be removed first by a pump; subsequently the neon when warmed can be similarly removed as the pure gas.

When these inert gases are examined by a spectroscope, they exhibit striking spectra. That is, when electric sparks are passed through a closed tube containing any of these gases and the light thereby produced is viewed through a spectroscope, many colored vertical lines are seen. Certain lines are conspicuous, *e.g.* the orange line in the case of helium, and by means of these and other lines it is possible to detect small quantities of these gases and to distinguish them from other gases, since no two spectra are exactly alike under given conditions. (For an account of the spectroscope and its application, see Chapter XXV.)

**Air is a mixture**, in spite of the fact that we speak of its "composition." Chemical compounds, as we have already learned, have two invariable characteristics; viz. (1) their constituents are in a fixed proportion, and (2) their formation and decomposition are usually attended by definite evidences of chemical action, such as light, heat, electrical phenomena, change of color, etc. The following facts show that air is a mixture of free gases: —

(1) The proportion of oxygen and nitrogen in the air is not fixed, but varies, though between very narrow and determinable limits.

(2) When nitrogen and oxygen are mixed in the proportions which form air, the product is exactly like air, but the act of mixing gives no evidence of chemical action.

(3) When air is dissolved in water, a greater proportion of oxygen than nitrogen dissolves; *i.e.* they dissolve as independent gases in proportions fixed by their intrinsic solubility and partial pressure. (See Solubility of Gases.) If the oxygen and nitrogen were combined in the air, the dissolved air would, of course, have the same composition as air itself.

(4) Oxygen and nitrogen distill independently from liquid air.

**Liquid air** is a mixture of the liquefied gases which constituted the air used. It is a milky liquid, owing to the presence of solid carbon dioxide and ice. If these solids are removed by filtering, the filtrate has a pale blue tint. It is intensely cold, and boils at about — 190° C. under atmospheric pressure. If a vessel is filled with liquid air, the latter boils vigorously, the surrounding air becomes very cold, frost gathers on the vessel, and in a short time the liquid air will have entirely disappeared into the air of the room. If, however, the liquid air is placed in a Dewar bulb, the evaporation is only slightly affected by changes of temperature.

The Dewar bulb (Fig. 14) consists of two flasks, one within the other, sealed together by an air-tight joint at the top; the space between the flasks is a vacuum. Sometimes the surfaces of the flasks are coated with silver, which reflects the heat and thereby retards the evaporation of the contents.

Liquid air, owing to its extremely low temperature, produces remarkable physical changes. A tin or iron vessel which has been cooled by liquid air is so brittle that it may often be crushed with the fingers. Nearly all plastic or soft substances, including many kinds of food, when immersed in liquid air become hard and brittle, leather being

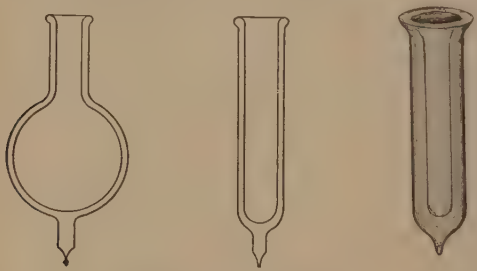


FIG. 14. — Dewar bulbs.

the only important exception. Mercury freezes so hard in liquid air that it can be used as a hammer to drive a nail. When liquid air is put in a teakettle standing on a block of ice the liquid air boils vigorously. If the kettle of liquid air is placed over a lighted Bunsen burner, frost and ice collect on the bottom of the kettle, because the intense cold of the kettle solidifies the water vapor and carbon dioxide which are the two main products of burning illuminating gas. If water is now poured into the kettle, the liquid air boils vigorously and the water is quickly frozen; the water is so much hotter than the liquid air that the latter boils more violently, and since its rapid evaporation causes absorption of heat, the water loses its heat and becomes ice. Ordinary liquid air is from one fifth to one half liquid oxygen, and will support combustion. A red-hot rod of steel or of carbon burns brilliantly in this cold liquid.

Numerous applications of liquid air have been proposed, but thus far they have not passed the experimental stage. It has been suggested that it be used as a refrigerant instead of ice, for ventilating and cooling rooms, as a blasting material, for removing diseased flesh from a wound, for destroying refuse, and as a commercial source of oxygen. The last use is based primarily on the fact that as liquid air evaporates the nitrogen passes off first, and in a short time relatively pure oxygen remains. (See Oxygen.)

A little liquid air was produced in 1883 with considerable labor and at an enormous expense. At present it is easily manufactured in large quantities at a comparatively low cost. Compressed air cooled by water is forced through a pipe to a valve. As it escapes through the valve, it expands and its temperature falls, because expansion is a cooling process. After expansion, the cold air is led back over the outer surface of the same pipe by which it came, whereupon it rapidly regains its former temperature. But in doing so it cools the pipe itself and the air within it. This latter air in turn expands and falls in temperature, but as it was cooler than the first portion before expansion, so it is colder than it after expansion. As the pressure within the pipe is maintained by a continuous supply of compressed air, the pipe becomes continually colder until finally the expanding air at the valve liquefies in part and is collected in a suitable receptacle.

**Liquefaction of Gases.** — In the first methods used to liquefy gases, the gas was subjected simultaneously to a great pressure and a low temperature. Thus, Faraday about 1823 liquefied chlorine gas by heating one arm of a sealed bent tube containing a chlorine compound after having placed the other end in a freezing mixture; the liberated chlorine being unable to escape was liquefied by

the pressure and low temperature. Other gases were liquefied by a similar method. A few, however, could not be liquefied, *e.g.* oxygen, hydrogen, and nitrogen, and these were called permanent gases. About 1870 it was shown that if these so-called permanent gases were cooled to a *sufficiently low temperature*, they could be liquefied if the pressure was also sufficiently great. It was found, furthermore, that each gas has a **critical temperature**, *i.e.* a temperature below which it must be cooled to produce liquefaction, no matter what the pressure. Thus, the critical temperature of oxygen is about $-118°$ C., that of carbon dioxide is about $+31°$ C., that of normal air is about $-140°$ C., and that of sulphur dioxide is about $+155.5°$ C. Obviously, critical temperatures vary between wide limits. The pressure which must be applied to liquefy a gas at its critical temperature is called its **critical pressure**. The latter value varies, but not between such wide limits as the critical temperature. It is about 58 atmospheres for oxygen, 15.3 for hydrogen, and 113 for ammonia ($NH_3$). As the temperature falls below the critical point, less pressure than the critical amount is needed for liquefaction, and if the temperature of the gas is reduced to the boiling point of the liquefied gas, no external pressure whatever is needed for liquefaction. Hence the essential point in liquefying most gases is the production of a sufficiently low temperature. This can be done in some cases by external application of cold, though in the case of gases having a low critical temperature, the required temperature is only produced by the expansion method, which is described under liquid air (see above).

If a liquefied gas can be cooled to a sufficiently low temperature, it becomes solid. Thus, Dewar by boiling liquid hydrogen under reduced pressure froze it to a foam-like solid, the temperature being about $-258°$ C.

## Nitrogen

**Occurrence.** — Nitrogen, besides comprising four fifths of the atmosphere, is a constituent of nitric acid and ammonia, and of many compounds related to them. It is also an essential constituent of animal and vegetable matter.

The name *nitrogen* was given to the gas by Chaptal from the fact that it is a constituent of niter, an old name of potassium nitrate.

**Preparation.** — Nitrogen can be obtained from the air by removing the oxygen by phosphorus. A tall jar is placed over burning phosphorus contained in a shallow dish floating in a large vessel of water. The oxygen combines with the phosphorus, leaving nitrogen, more or less pure, in the jar. Other methods may be used, such as passing air over heated copper, or decomposing ammonium nitrite by heat. It can readily be prepared in the laboratory by applying heat gently to a mixture of sodium nitrite, ammonium chloride, and water.

**Additional Properties.** — In addition to its inertness, already mentioned, nitrogen is a little lighter than air, and is very sparingly soluble in water. Its density is .972 (air = 1). One liter at 0° C. and 760 mm. weighs 1.2507 gm. One hundred liters of water dissolve only about 1.5 l. at the ordinary temperature. The critical temperature is about −146° C. Liquid nitrogen boils at −195.5° C. under ordinary atmospheric pressure, and solid nitrogen melts at about −214° C.

It combines with magnesium and a few other metals at a red heat, forming nitrides, *e.g.* magnesium nitride ($Mg_3N_2$). Electric sparks cause nitrogen to combine with oxygen and with hydrogen, forming nitric acid and ammonia; hence these substances or others related to them are often found in the rain which falls during a thunder storm.

**Relation of Nitrogen to Life.** — Oxygen, carbon dioxide, and water vapor are essentially related to the life of plants and animals. Nitrogen is also vitally connected with different forms of life. Atmospheric nitrogen merely dilutes the oxygen. Although we live in an atmosphere containing such a large proportion of nitrogen, we cannot assimilate it. According to a reliable authority, "the air as it leaves the lungs contains 79.5 per cent of nitrogen," and hence cannot become a part of the body. Yet all flesh contains nitrogen, and certain rejected waste products of animals

FIG. 15. — A leguminous plant (the hairy vetch) with (*B*) and without (*A*) nodules on the roots.

contain considerable combined nitrogen. The nitrogen needed by animals must be in combination to become available. And it is taken in the form of nitrogenous food such as lean meat, fish, wheat and other grains.

Most plants take up combined nitrogen from the soil in the form of nitrates (compounds derived from nitric acid) or of ammonia. Hence combined nitrogen is being con-

stantly taken from the soil, and in order to preserve the fertility of the soil, nitrogen must be supplied. This is done by allowing nitrogenous organic matter to decay upon the soil, or by adding to the soil a fertilizer, which is a mixture containing nitrogen compounds. Recently it has been shown that leguminous plants, such as peas, beans, and clover, assimilate free nitrogen directly from the air by means of bacteria which are in nodules on their roots (Fig. 15).

### Problems and Exercises

1. If a man inhales 18 cu. ft. of air an hour, what volume of oxygen does he use up in 24 hr.?

2. What is the weight of air in a room, $6 \times 6 \times 3$ m., if a liter of the air weighs 1.3 gm.?

3. A mixture of 25 cc. of air and 50 cc. of hydrogen is exploded. The residue measures 60.3 cc. What per cent of oxygen did this sample of air contain?

4. How many kilograms of pure air are needed to yield 100 kg. of oxygen?

5. Dumas and Boussingault, in 1841, found in a sample of air 12.373 gm. of nitrogen and 3.68 gm. of oxygen. What per cent of each was found?

6. What is the weight at 0° C. and 760 mm. of (*a*) 1000 cc. of dry air, of (*b*) 750 l., (*c*) 1750 cc., (*d*) 850 cu. m.?

7. Calculate the percentage composition of (*a*) magnetic oxide of iron ($Fe_3O_4$), (*b*) crystallized sodium carbonate ($Na_2CO_3 . 10\ H_2O$).

8. How many grams of argon can be obtained from 1500 kg. of normal air? How many cubic centimeters from 1500 l.?

9. How many grams of copper oxide (CuO) are formed by passing 1728 gm. of normal air over pure copper? How many grams of magnesium nitride ($Mg_3N_2$) by passing the residual gas over red-hot magnesium? How many grams of gas remain? Equations are $Cu + O = CuO$ and $3\ Mg + 2\ N = Mg_3N_2$.

10. Write equations for the following reactions: (*a*) Phosphorus pentoxide and water form phosphoric acid ($H_3PO_4$). (*b*) Copper oxide (CuO) and hydrogen form copper and water.

# CHAPTER IX

## Solution — Theory of Electrolytic Dissociation

**Introduction.** — Many facts about solutions have already been stated (see Chapter V). The present chapter is a continuation of the discussion of solutions with special reference to the theory of their nature and the interpretation of certain phenomena by this theory. The term *solution* will be restricted to aqueous solutions, *i.e.* those in which water is the solvent.

**General Properties of Solutions.** — It is very desirable to recall at this point certain properties of solutions. First, the solubility of the solute in the solvent varies widely and is generally increased by rise of temperature until it reaches a limit, thereby giving the phenomena connected with unsaturation, saturation, and supersaturation. Second, the solute in most cases can be recovered unchanged by evaporating, cooling, or distilling the solution. Third, the solution often contains the solute in an especially favorable condition for chemical action. Finally, solutions have a definite boiling point, freezing point, and vapor pressure, which differ from the corresponding values of the solvent.

**Behavior of Solutions toward an Electric Current.** — Pure water and pure dry, solid sodium chloride do not appreciably permit the passage of an electric current. But a solution of sodium chloride is an excellent conductor of electricity, and the same is true of a solution of hydrochloric acid and of sodium hydroxide. On the other hand, sugar is a non-conductor, both in solution and in the solid state. In a word,

solutions of certain substances conduct electricity, while solutions of others do not. Hence solutions can be divided on this basis into two classes, viz.: (1) electrolytic solutions, or those which conduct electricity, and (2) non-electrolytic solutions, or those which do not conduct electricity. Substances whose solutions are electrolytic are called **electrolytes**, and those whose solutions are not electrolytic are called **non-electrolytes**. Each class has characteristic properties. But electrolytes possess certain conspicuous properties which are not exhibited by non-electrolytes, and it was the study of these characteristic properties that led to the proposal of the present theory of solutions. It is called the theory of electrolytic dissociation and was proposed by the Swedish physicist Arrhenius in 1887; its general adoption has been hastened by the work of Van't Hoff, Ostwald, and Nernst.

**Theory of Electrolytic Dissociation.** — It was believed for many years that the molecules of a dissolved substance were distributed unchanged throughout the solvent. It was also believed that the molecules of certain dissolved substances combined to some degree with the molecules of the solvent. Evidence is fast accumulating which indicates that in many solutions the solute is in the form of molecules, while in others the solvent does unite with the solute or some of its constituents. The present theory of solutions differs from these by offering an explanation of solution which is more comprehensive. Briefly, the **theory of electrolytic dissociation** assumes (1) that molecules of electrolytes when dissolved in water break up to a varying degree into independent particles charged with electricity, and (2) that the nature and number of these electrically charged particles determine to a large extent certain physical and chemical properties of solutions.

Before stating the facts on which the theory is based, it will be necessary to expand the two assumptions and to define several terms. The breaking up of certain substances when in aqueous solution is called electrolytic dissociation, or **ionization**. The independent particles are called **ions**. Thus, when sodium chloride is dissolved in water, some of its molecules dissociate into sodium ions and chlorine ions. Each ion is a portion of a molecule and is charged with electricity. Two kinds of ions are present in every electrolytic solution, viz. electro-positive ions, or **cations**, and electro-negative ions, or **anions**. Ions, although formed by the dissociation of molecules, are not identical with atoms, but differ mainly in having a charge of electricity. For example, when sodium chloride is dissolved in water, the electro-positive sodium ions move about in the water without producing any apparent chemical change; but ordinary sodium interacts violently with water, as we have already seen. Similarly, the chlorine ions circulate freely in water and exhibit none of the effects of gaseous chlorine upon water. In a word, in such a solution the sodium ions and chlorine ions exist side by side without any apparent decomposition of the water or any apparent tendency to combine with each other. The properties of ions, as already stated, are mainly due to their electric charges, and **ions** may be defined as electrically charged atoms or atomic groups. It is customary to represent ions by chemical symbols supplemented by the sign which designates the kind of electric charge. Thus, the ions formed by the dissociation of sodium chloride are $Na^+$ and $Cl^-$, while potassium nitrate yields $K^+$ and $NO_3^-$. A solution of sodium chloride gives no evidence of electricity. In general, solutions of electrolytes are electrically neutral; *i.e.* although they allow an electric current to pass through them when supplied from some external source such as a battery or dynamo, the solution itself is electrically neutral.

It therefore follows that the sum of the electric charges of the positive ions equals the sum of the electric charges of the negative ions. The ions balance each other electrically. Thus, in the case of sodium chloride solution, the number of sodium ions equals the number of chlorine ions and the sum of the positive charges on the sodium ions equals the sum of the negative charges on the chlorine ions. In the case of calcium chloride ($CaCl_2$), each molecule dissociates into two chlorine ions and one calcium ion; but since the sum of each kind of electric charges must be the same, each calcium ion must carry twice the charge which is on each chlorine ion. Hence the calcium ions are designated as $Ca^{++}$ and the chlorine ions as $2\ Cl^-$. A unit charge of electricity is indicated by the single sign, and multiples by the proper number. For example, the sodium ion is $Na^+$, the common copper ion is $Cu^{++}$, the aluminium ion is $Al^{+++}$, the sulphate ion is $SO_4^{--}$, and the nitrate ion is $NO_3^-$. The degree of dissociation varies with the concentration and with the electrolyte. The greater the dilution, the greater the dissociation. Conversely, dissociation is decreased by decreasing the volume of the solvent; the ions tend to unite, forming undissociated molecules which can be ultimately obtained as a mass of the original substance by evaporation. Consequently, a solution contains undissociated molecules as well as ions, depending upon the substance and the concentration of the solution. Experiment shows that the chemical behavior of a dissolved substance often depends largely on the extent of the dissociation of the molecules into ions.

As previously stated, only certain substances are electrolytes. These are acids, bases, and salts. The general properties of these substances are discussed in Chapter X and their special characteristics are treated under the individual compounds. It is sufficient for our present purpose to regard them as a single class of substances which dissociate

in solution into ions. That is, ions are in the solutions of the familiar acids like sulphuric, hydrochloric, and nitric, the familiar bases like sodium hydroxide and potassium hydroxide, and the familiar salts like potassium chlorate, sodium chloride, sodium sulphate, and many others which will soon be described. Sugar, alcohol, and other compounds not so familiar do not dissociate into ions when dissolved in water and their solutions do not conduct electricity. Nevertheless, such solutions have specific and instructive properties, especially when compared with the properties of electrolytic solutions.

**Properties of Electrolytes and Non-electrolytes.** — The theory of electrolytic dissociation, which has just been discussed, is based on many facts which have accumulated as the outcome of a comprehensive study of the properties of solutions, both electrolytic and non-electrolytic. These facts will now be presented. Careful distinction should be drawn between the statements in the paragraphs immediately preceding and those about to be made. The preceding concerned the theory of electrolytic dissociation. The forthcoming concern facts and laws derived from experiment and interpreted by the theory.

(a) *Osmotic Pressure.* — A dissolved substance, sooner or later, becomes uniformly distributed throughout the water, thereby producing the homogeneous mixture which we call a solution. That the distribution of the solute is uniform may be learned by testing the concentration at different points in the solution. Thus, if a vessel containing a little sodium chloride is filled with water, all parts, including the upper part, will soon taste salty; the same phenomenon is strikingly exhibited by substances like copper sulphate and potassium permanganate which produce colored solutions. That is, the particles of the dissolved solid move

about freely in the solvent and behave analogously to a gas when it is permitted to diffuse through the air or another gas. Now when this movement of the solute in a solution is opposed by a suitable device, it is found that the solute exerts a pressure. This pressure is called **osmotic pressure.** It can best be observed and measured by an apparatus whose essential part is a porous porcelain vessel whose walls constitute a semi-permeable membrane, *i.e.* a partition which permits the solvent to flow in and out freely but prevents the escape of the solute. The experiment is performed substantially as follows: A cell containing such a semi-permeable membrane within its walls and provided with a measuring tube is filled with a sugar solution and immersed in water. Water flows into the cell through the semi-permeable membrane until the pressure of the water inside and outside is the same. As the experiment proceeds the measuring tube reveals pressure inside the cell. This excess of pressure is not caused by the water, because that can escape through the semi-permeable membrane; therefore it is due to the osmotic pressure of the sugar particles whose escape is prevented by the membrane. Determinations of the value of osmotic pressure show that it is proportional to the concentration of the solution (if the temperature is constant). For example, the osmotic pressure of solutions of sugar having concentrations in the ratio 1 : 2 : 5 was found to be respectively 4.83, 9.72, and 24.46 atmospheres. Again, osmotic pressure varies with increase of temperature, the increment being 1/273 of the osmotic pressure at 0° C. for the rise of each degree of temperature. Stated in another way, osmotic pressure is proportional to the absolute temperature (if the volume is kept constant). For example, it was found that a certain sugar solution had an osmotic pressure of 510 mm. at 14.2° C. or 287.2° abs. and a pressure of 544 mm. at 32° C. or 305° abs. The theoretical values of the

osmotic pressure are 510 mm. and 542 mm., the slight variation in one case being less than the error due to the experimental work. Furthermore, if a gram-molecular weight (*i.e.* a number of grams equal to the numerical value of the molecular weight) of substances giving non-electrolytic solutions is dissolved in equal volumes of water, the osmotic pressure of each solution is the same. The gram-molecular weight is often called a mole — a convenient term which will be hereafter used. For example, one mole (342 gm.) of cane sugar ($C_{12}H_{22}O_{11}$) and one mole (58 gm.) of acetone ($C_3H_6O$) dissolved in equal volumes of water have the same osmotic pressure under parallel conditions.

The osmotic pressure of an electrolytic solution is found to be greater than that of a non-electrolytic solution under the same conditions. The excess of pressure varies somewhat with the conditions, *i.e.* with concentration, temperature, and the substance. Nevertheless, the difference between the normal and the abnormal osmotic pressure is conspicuously large in the case of many substances yielding electrolytic solutions, these substances being acids, bases, and salts. Thus, a solution of potassium chloride has an osmotic pressure 1.88 times that of a corresponding sugar solution, while a calcium chloride solution has a pressure about 2.5 times. This discrepancy between the values of the osmotic pressure of non-electrolytic and electrolytic solutions is readily explained, if the facts are interpreted by the theory of electrolytic dissociation. According to this theory a non-electrolytic solution contains only molecules and an electrolytic solution contains both ions and molecules. Now osmotic pressure is believed to be due to the independent particles of the solute in solution, and the amount of pressure is determined by the number of particles in a given volume. Hence, when equivalent solutions are used, the electrolytic solution contains more particles than the non-electrolytic

because some of the molecules of the electrolytic solution are dissociated into ions. Facts and theory agree as far as osmotic pressure is concerned.

(b) *Freezing Point and Boiling Point of Solutions.* — In the preliminary discussion of the properties of solutions given in Chapter V, it was stated that the freezing point of a solution is lower than the freezing point of the solvent and that the depression of the freezing point is proportional to the concentration of the solution. These facts can be expressed by a concrete case, thus: —

DEPRESSION OF THE FREEZING POINT

| SOLVENT | SOLUTE | FREEZING POINT | DEPRESSION |
|---|---|---|---|
| 100 gm. | 11.4 gm. sugar | — .62° C. | .62 |
| water | 22.8 gm. | —1.23° C. | 2 × .62 (approx.) |
| in each case | 34.2 gm. | —1.85° C. | 3 × .62 (approx.) |

Furthermore, experiment shows that the freezing point of water is depressed the same number of degrees, if 1000 gm. of water contain a mole of certain solutes (*i.e.* a number of grams numerically equal to the molecular weight). Thus, the freezing point of water is depressed about 1.89° C. by a solution of 342 gm. of cane sugar ($C_{12}H_{22}O_{11}$) and 58 gm. of acetone ($C_3H_6O$), each dissolved in 1000 gm. of water. This uniform behavior is not well exhibited, however, unless the solutions are dilute and involve no chemical action between solvent and solute. On the other hand, when solutions of electrolytes, *i.e.* acids, bases, and salts, are experimented with, the freezing point is lower than that produced by non-electrolytes under the same experimental conditions. Moreover, the depression is not uniform for all electrolytic solutions under uniform conditions. For example, a solution containing a mole of sodium chloride (*i.e.* 58.5 gm.) to the

liter depresses the freezing point of water about 3.5° C., or nearly twice the amount produced by a cane sugar solution of equivalent concentration. This exceptional behavior of solutions of acids, bases, and salts can be explained as in the case of osmotic pressure. Solutions of non-electrolytes contain only molecules, while solutions of electrolytes contain ions into which some of the molecules have dissociated. Hence the number of independent particles (molecules and ions) in the electrolytic solution is greater than in the non-electrolytic solution. Ions and molecules act alike on the freezing point of a solution, and the larger the number of particles, the greater the depression. This deduction is further confirmed by the fact that electrolytic solutions in which a large proportion of molecules is dissociated show a relatively greater depression than those in which the dissociation is limited — the degree of dissociation being found by an independent experiment.

Analogous statements can be made about the elevation of the boiling point of solutions. That is, (1) the boiling point of a solution is higher than that of the solvent, (2) the elevation of the boiling point is proportional to the concentration, and (3) the elevation is the same (*i.e.* .52° C.) in the case of all non-electrolytic solutions containing a mole of the solute in 1000 gm. of water. But solutions of acids, bases, and salts behave exceptionally. They boil at a higher temperature than non-electrolytic solutions of the same concentration. The explanation offered by the theory of electrolytic dissociation is the same as in the preceding cases, viz. dissociation of some of the molecules into ions, which affect the boiling point in the same way as the molecules themselves.

(c) *Electrolysis of Solutions.* — Electrolysis is the series of changes accompanying the passage of an electric current through a solution. It is accomplished in an electrolytic cell. This piece of apparatus consists of three essential parts —

the electrolytic solution, the containing vessel, and two electrodes which convey the electric current to and from the solution. A simple form of such a cell is shown in Figure 16. It is customary to speak of the current as entering the solution by the anode or positive electrode and as leaving by the cathode or negative electrode. Both the electrolytic cell and the ordinary voltaic cell are fully described in Chapter XI, though a general idea of the electrolytic cell serves our present need.

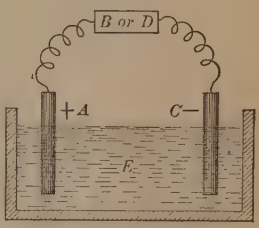



FIG. 16. — Electrolytic cell. $A$ and $C$ are the electrodes which dip into the electrolytic solution ($E$); $B$ or $D$ is the battery or dynamo which provides the electricity.

When a concentrated solution of hydrochloric acid gas (commonly called simply hydrochloric acid) is put into an electrolytic cell and subjected to the action of an electric current, two gases are liberated, — hydrogen at the cathode and chlorine at the anode. This is a very simple illustration of electrolysis. Let us interpret it by the theory of electrolytic dissociation. When hydrochloric acid gas is dissolved in water, hydrogen ions ($H^+$) and chlorine ions ($Cl^-$) are immediately formed by the dissociation of some of the molecules of hydrochloric acid (HCl). These ions are formed in the solution as soon as the acid dissolves and before the electric current is connected with the cell. As soon as the current is turned on, however, the electrodes at once become charged with electricity — the anode assuming a positive charge and the cathode a negative charge. Now according to a principle established many years ago, bodies charged with like kinds of electricity repel each other and bodies charged with unlike kinds attract each other. Consequently the anions or electro-negative ions move toward the anode or electro-positive

electrode, while the cations or electro-positive ions move toward the cathode or electro-negative electrode, or briefly, "anions to anode, cations to cathode." This migration of the ions, as it is called, toward their respective poles is shown diagrammatically in Figure 17. As soon as the ions reach their electrodes, they act in accordance with another long-established principle; that is, they give up their electric charges. In other words, when the electro-positive cations of hydrogen touch the electro-negative cathode, the electric charges are neutralized. Electric charges are constantly renewed on the cathode by the battery or dynamo, but the hydrogen ions once deprived of their electric charges do not regain them and immediately become ordinary, uncharged hydrogen atoms, which combine and escape as molecules of hydrogen gas. Similarly, the electro-negative anions of chlorine migrate to the electro-positive anode, lose their charges, become chlorine atoms, and ultimately escape as chlorine gas. All cases of electrolysis are not as simple as this one, but it serves admirably as an introductory illustration. It should be noted that the electric current does not tear the molecules apart, as was once supposed. The molecules of hydrochloric acid that dissociate are already dissociated before the electric current is introduced. The current upsets the electrical equilibrium between the ions, so to speak, and they start at once on a migration toward their proper electrodes where they lose their charges and become ordinary, uncharged atoms or atomic groups. Careful and extended experiments have not only demonstrated the actual movement of ions, but have deter-

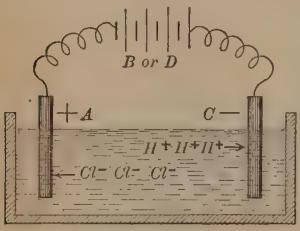



FIG. 17. — Movement of ions in an electrolytic cell.

mined the rate of migration in many cases. Non-electrolytic solutions do not conduct electricity, because, according to the theory of electrolytic dissociation, they contain no ions. In this connection it is appropriate to emphasize the fact that only those solutions conduct electricity that have been found by other methods to contain ions.

Electrolysis is often a complicated process, since the regenerated atoms and atomic groups may interact chemically with the constituents of the solution and sometimes with each other or with the electrodes. The electrolysis of copper sulphate furnishes a typical illustration. The ions of a copper sulphate solution are copper ions ($Cu^{++}$) and sulphate ions ($SO_4^{--}$). When this solution is electrolyzed, the copper ions ($Cu^{++}$) lose their electric charges at the cathode, become copper atoms (Cu), and adhere as metallic copper to the cathode. The sulphate ions ($SO_4^{--}$) lose their electric charges at the anode and become ordinary, uncharged atomic groups ($SO_4$). But this group of atoms is chemically unstable, and immediately interacts with the water around the anode, forming sulphuric acid ($H_2SO_4$) and oxygen (O). The oxygen escapes, but the sulphuric acid mingles with the solution and dissociates into its ions. Similarly, a solution of sodium sulphate when undergoing electrolysis yields sulphuric acid at the anode and sodium hydroxide (NaOH) at the cathode; the electrolyte itself (sodium sulphate) furnishes directly only sodium and sulphate ions, which lose their charges at the electrodes, and by their subsequent chemical interaction with the water give the final result just stated.

The so-called electrolysis of water is readily interpreted by the theory of electrolytic dissociation. Water itself does not conduct electricity to an extent which is comparable with the behavior of an electrolytic solution, because water dissociates only inappreciably and gives therefore an exceed-

ingly small number of ions. A solution of sulphuric acid contains hydrogen ions ($H^+H^+$) and sulphate ions ($SO_4^{--}$). When a current is passed through this solution, hydrogen ions migrate to the cathode, lose their electric charges, become hydrogen atoms, and eventually escape as hydrogen gas; the $SO_4$-ions migrate to the anode, lose their electric charges, become $SO_4$-groups, and interact with the water to form sulphuric acid and oxygen. The oxygen escapes as a gas, while the sulphuric acid dissociates into its ions. The water, therefore, is not split up directly into hydrogen and oxygen, as was formerly supposed. The two liberated gases are produced by the joint operations of electrolysis and subsequent chemical action, but the gases would not be liberated at all unless the ionization of the sulphuric acid had previously occurred in the solution.

Electrolysis is a broad subject, and is not limited to aqueous solutions. In subsequent chapters frequent reference will be made to the electrolysis of molten substances, especially to the industrial applications which have become so important. Enough has been set forth at present, however, to show that the facts thus far revealed by electrolysis are in harmony with the theory of electrolytic dissociation.

(d) *Chemical Behavior of Electrolytic Solutions.* — It has been pointed out that chemical action is often dependent upon the presence of water. Dry compounds like potassium chloride (KCl) and silver nitrate ($AgNO_3$) do not interact chemically, but if their solutions are mixed, a precipitate of silver chloride (AgCl) is immediately produced. On the other hand, there is no chemical action manifested when solutions of potassium chlorate ($KClO_3$) and silver nitrate are mixed, despite the fact that chlorine is a constituent of potassium chlorate. Furthermore, *any* chloride in solution will interact with silver nitrate in solution and produce a precipitate of silver chloride. These facts are typical of

electrolytic solutions. Interpreted by the theory of electrolytic dissociation, they mean that reactions in solutions are due to some extent to ions. Dry or undissolved electrolytes do not interact, because no ions are present, but in the case of dissolved electrolytes certain ions at once seek each other out in accordance with the fundamental principles of chemical action. If this action results in the formation of an insoluble compound, like silver chloride, this factor is removed from the scene of action as a precipitate and serves as visual evidence of the chemical change. Often ions are produced which cannot enter into chemical combination. Thus, a potassium chlorate solution contains potassium ions ($K^+$) and chlorate ions (($ClO_3^-$), and when silver nitrate solution is added, the solution contains four kinds of ions, — potassium ions ($K^+$), chlorate ions ($ClO_3^-$), silver ions ($Ag^+$), and nitrate ions ($NO_3^-$). But all compounds which might be formed by the various combinations of these ions are soluble. Hence the ions remain as such in the solution. It is for this reason that silver nitrate is effective in testing for hydrochloric acid or a soluble chloride, but not for other compounds containing chlorine, such as potassium chlorate ($KClO_3$) and chloroform ($CHCl_3$). Strictly speaking, the test is for chlorine ions or ionic chlorine, not for the element chlorine; and since the solutions of potassium chlorate and chloroform contain no ionic chlorine, the test fails with these compounds. Similarly, sulphuric acid and all soluble sulphates form insoluble barium sulphate ($BaSO_4$) when added to a solution of barium chloride (or any other soluble barium compound), because the sulphuric acid and sulphate solutions contain sulphate ions ($SO_4^{--}$), which combine with the barium ions ($Ba^{++}$) in the barium chloride solution. But other sulphur compounds, such as sulphides, sulphites, and thiosulphates, do not form barium sulphate when added to barium chloride solution, because solutions

of these compounds do not contain sulphate ions. It is clear from the above statements why a single test (*i.e.* the precipitation of barium sulphate) is applicable to sulphuric acid and *all* soluble sulphates. All contain in solution a common ion ($SO_4^{--}$).

Other properties besides the formation of precipitates are ascribed to ions and are often used as tests. Thus, the sour taste of all acids is attributed to hydrogen ions ($H^+$), which are common to acids. The color of solutions is also due to ions. Most ions are colorless, while solutions having a common colored ion have the same color. Thus, copper ions ($Cu^{++}$) are blue, and solutions containing such ions are blue, irrespective of the color of the undissolved copper compound. Cobalt ions ($Co^{++}$) are pink, and nickel ions ($Ni^{++}$) are green — colors usually exhibited by solutions of compounds of these elements. The migration of ions is often studied by means of colored ions.

**Common Ions.** — Ions, as already stated, are electrically charged atoms or atomic groups. It is rather difficult for a beginner to determine what ions are present in a solution. The problem is simplified somewhat if the following general statements are borne in mind. (*a*) Hydrogen and metals form simple cations. (*b*) Non-metals (except hydrogen) form simple anions. (*c*) Some metals (*e.g.* Cr and Mn) and several non-metals (*e.g.* C, N, S, P) form compound ions — usually anions; *e.g.* $HCO_3^-$, $NO_3^-$, $HSO_4^-$, $H_2PO_4^-$, $CrO_4^{--}$, $MnO_4^-$ (note also $OH^-$ and $NH_4^+$). Certain elements likewise form complex ions; *e.g.* the silver-cyanogen ion ($(Ag(CN)_2)^-$), the silver-ammonia ion ($(Ag(NH_3)_2)^+$), and the copper-ammonia ion ($(Cu(NH_3)_4)^{++}$). The ions formed by the dissociation of the common compounds of the familiar elements are shown in the following: —

TABLE OF COMMON IONS

| ELEMENT OR GROUP | ION | ELEMENT OR GROUP | ION | ELEMENT OR GROUP | ION |
|---|---|---|---|---|---|
| Hydrogen . . | $H^+$ | Calcium . . | $Ca^{++}$ | Aluminium . | $Al^{+++}$ |
| Sodium . . . | $Na^+$ | Barium . . . | $Ba^{++}$ | Antimony . | $Sb^{+++}$ |
| Potassium . . | $K^+$ | Copper . . . | $Cu^{++}$ | Bismuth . . | $Bi^{+++}$ |
| Silver . . . . | $Ag^+$ | Zinc . . . . | $Zn^{++}$ | Iron (ic) . . | $Fe^{+++}$ |
| Ammonium . | $NH_4^+$ | Magnesium . | $Mg^{++}$ | Tin (ic) . . . | $Sn^{++++}$ |
| Mercury (ous) | $Hg^+$ | Lead . . . . | $Pb^{++}$ | | |
| Chlorine . . . | $Cl^-$ | Iron (ous) . | $Fe^{++}$ | | |
| Bromine . . . | $Br^-$ | Mercury (ic) | $Hg^{++}$ | | |
| Iodine . . . . | $I^-$ | Tin (ous) . | $Sn^{++}$ | | |
| Nitrate . . . . | $NO_3^-$ | Sulphate . . | $SO_4^{--}$ | | |
| Chlorate . . . | $ClO_3^-$ | Sulphide . . | $S^{--}$ | | |
| Hydroxyl . . | $OH^-$ | Carbonate . | $CO_3^{--}$ | | |
| | | Chromate . | $CrO_4^{--}$ | | |
| | | Dichromate | $Cr_2O_7^{--}$ | | |

Many deductions arising from this rather compact table will be considered in the succeeding pages.

**Summary.** — The salient points discussed in this chapter may be summarized as follows: The properties of a solution are mainly dependent upon the solute and its condition in the solvent. Such properties as osmotic pressure, freezing point, and boiling point, are influenced by the number of independent particles present in the solution. When these three properties are measured independently in a given solution, the values agree. But when the values are compared under parallel conditions of measurement, it is found that electrolytes in solution yield a larger number of independent, individual particles than non-electrolytes; *i.e.* in electrolytic solutions some of the molecules of the electrolytes dissociate into ions. These ions are electrically charged atoms or atomic groups. Physically they act much like molecules.

Furthermore, solutions of electrolytes differ from solutions of non-electrolytes in conducting electricity and exhibiting marked chemical activity. A study of these two characteristics confirms the assumption of the existence of electrically charged and chemically active particles in the solution.

**Conclusion.** — The theory of electrolytic dissociation as outlined in the foregoing pages is not an adequate explanation of all the facts of solution. It applies chiefly to dilute aqueous solutions of three classes of substances. Doubtless the present form of the theory will sometime be modified to cover certain facts not at present within its scope.

### Exercises

1. Write out the formulas of the ions formed when the following compounds are dissolved separately in considerable water: Potassium chloride, silver nitrate, sodium chlorate, ammonium sulphate, copper nitrate, calcium chloride, zinc sulphate, potassium dichromate, calcium hydroxide.

2. Write the equations for the following by applying the method for making equations outlined in Chapter VII: (*a*) Iron and sulphur combine in the ratio of 7 to 4. (*b*) Ammonia gas and hydrochloric acid gas form ammonium chloride. (*c*) Magnesium and hydrochloric acid form hydrogen and magnesium chloride.

# CHAPTER X

## Acids, Bases, and Salts — Neutralization

**Introduction.** — Many chemical compounds fall naturally into one of three groups, long known as acids, bases, and salts. Each group has its characteristic properties, though the groups are closely related and sometimes overlap. Many familiar substances belong to these groups.

**Acids.** — The common acids are sulphuric acid ($H_2SO_4$), hydrochloric acid (HCl), nitric acid ($HNO_3$), and acetic acid ($C_2H_4O_2$). Many acids are liquid, as sulphuric and nitric; a few are gases, as hydrochloric; others are solid, as tartaric, citric, oxalic. Most acids are rather soluble in water, and such solutions are popularly called acids. These solutions may be dilute or concentrated, and the general properties vary somewhat with the concentration. Concentrated acids are usually corrosive and should be handled with caution, even when one is familiar with their properties.

Many familiar substances are acids or contain them. Vinegar, pickles, and similar relishes contain dilute acetic acid. Lemon juice is mainly citric acid. Sour milk contains lactic acid. Unripe fruits, sour bread, and sour wines contain acids. "Soda water" is a solution of carbonic acid (or more accurately carbon dioxide), and "acid phosphate" is a solution of a sour calcium phosphate.

**Properties of Acids.** — (1) Acids, if dissolved in water, usually have a sour taste. The early chemists detected this fact, and the term *acid* (from the Latin word *acidus*,

sour) emphasizes this property. (2) Solutions of acids redden the coloring matter called litmus. Solutions which act thus on blue litmus are described as acid, as containing an acid, or as having an **acid reaction**. (3) Most acids liberate free hydrogen gas when their solutions interact with metals. (4) Solutions of acids conduct electricity.

**Composition of Acids.** — All acids contain hydrogen, which is liberated in the free state when certain metals and acids interact. Most acids contain oxygen. For many years it was thought that oxygen was an essential component of all acids, and the name *oxygen* (derived from Greek words meaning "acid producer") was given to this element by Lavoisier because of this belief. (See Discovery of Oxygen.) We know now that hydrogen, not oxygen, is the essential constituent of all acids. Another necessary constituent of acids is a non-metallic element like nitrogen or sulphur. For this reason it is sometimes convenient to think of **non-metals** as the elements which form acids. Thus, sulphuric acid contains sulphur, besides hydrogen and oxygen; while hydrochloric acid contains only chlorine, besides hydrogen. The important non-metals which form familiar acids are boron, carbon, silicon, nitrogen, phosphorus, sulphur, fluorine, chlorine, bromine, and iodine.

**Definition of an Acid.** — For many years an acid was defined as a compound producing a sour solution which reddens blue litmus, or as a compound which interacts chemically with a base, thereby forming a salt, or as a compound containing hydrogen which can be replaced by a metal. These definitions emphasize certain properties of acids, but they are not inclusive. According to the theory of electrolytic dissociation, an acid is a compound whose solution contains hydrogen ions ($H^+$). The sour taste, behavior toward litmus, and liberation of hydrogen are due

to the hydrogen ions which are common to all solutions of acids.

**Bases.** — The common bases are sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide ($NH_4OH$), and calcium hydroxide ($Ca(OH)_2$). They are soluble in water, and such solutions are called bases; solutions of the very soluble bases (sodium hydroxide and potassium hydroxide) are often called **alkalies**. Alkalies, like concentrated acids, are corrosive, and should be handled carefully. Concentrated solutions of sodium and potassium hydroxides are very corrosive, and for this reason are called caustic alkalies (from the Latin *causticus*, burning).

Bases are components of familiar substances. Thus, ammonia is a solution of ammonium hydroxide. Lime-water and baryta water are solutions of the sparingly soluble bases calcium hydroxide and barium hydroxide ($Ba(OH)_2$) respectively. Lye is a concentrated solution of sodium hydroxide or potassium hydroxide (or both).

**Properties of Bases.** — (1) Strong, soluble bases have a bitter, often biting, taste; many, especially the very soluble ones, have a slippery feeling. (2) Soluble bases turn red litmus blue. Substances which act thus on red litmus are described as basic or alkaline, as having an **alkaline reaction**, or as containing a base. (3) Solutions of bases conduct electricity.

**Composition of Bases.** — All bases contain hydrogen and oxygen. They also contain a metal, such as sodium. The hydrogen and oxygen are the invariable constituents. But it is often convenient to regard **metals** as the elements which form bases, just as the non-metals form acids. Thus, the base sodium hydroxide is a compound of the metal sodium with hydrogen and oxygen. The important metals which

form familiar bases are sodium, potassium, calcium, and barium.

**Definition of a Base.** — A base was formerly defined as any compound which has a bitter taste, turns red litmus blue, and interacts chemically with an acid, thereby forming a salt. This definition emphasizes certain properties of a base, but it is defective. According to the theory of electrolytic dissociation, a base is a compound whose solution contains hydroxyl ions ($OH^-$). The metal is not the constituent which gives a base its characteristic properties. These are due to the hydroxyl ions which are common to all solutions of bases.

**Salts.** — This is a large and varied class of compounds. The most familiar member is sodium chloride ($NaCl$). It is common salt or table salt, and has been known for ages. Doubtless this class of chemical compounds received its name from the general resemblance many of them bear to common salt. Most salts are solids and are soluble in water, although the solubility varies between wide limits.

**Properties of Salts.** — (1) Salts often have the well-known salty taste, though some are bitter, others are astringent, and a few have no characteristic taste. Certain salts have a sour taste. (2) Salts do not act uniformly on litmus. Some turn the red to blue, others turn the blue to red, and many have no action whatever on litmus. Those salts whose solutions do not respond to the litmus test are said to be neutral or to have a **neutral reaction**. This indifference to litmus is not a decisive test for a salt, since many other substances, water for example, have no action on litmus. The term *neutral* is applied to substances which do not change the color of litmus, whether or not they are salts or contain salts. (3) Solutions of salts conduct electricity.

**Composition of Salts.** — Salts contain invariably a metal and a non-metal (which is not hydrogen or oxygen). Most salts also contain oxygen. Thus, potassium nitrate contains the metal potassium and the non-metal nitrogen, besides oxygen; while potassium chloride contains potassium and the non-metal chlorine, but no oxygen. A few salts contain hydrogen besides the characteristic metal and non-metal. Thus, sodium bicarbonate contains hydrogen besides the metal sodium, the non-metal carbon, and the non-metal oxygen. These rather general statements indicate the great variety of salts. Salts will soon be further discussed.

**Neutralization.** — The nature and interrelation of acids, bases, and salts are shown clearly by their chemical relations. When a solution of an acid and a base are mixed in the proper proportion, they interact completely. The final solution has none of the properties of an acid or a base, but it has the properties characteristic of a salt. That is, the acid and base destroy more or less completely the marked properties of each other and produce a salt, the latter being a compound which has few, if any, of the properties of the original acid and base. The acid and base neutralize each other. An illustration will make this point clear. When hydrochloric acid and sodium hydroxide interact, sodium chloride and water are formed. The chemical change can be written thus: —

| $HCl$ | + | $NaOH$ | = | $NaCl$ | + | $H_2O$ |
|---|---|---|---|---|---|---|
| Hydrochloric Acid | | Sodium Hydroxide | | Sodium Chloride | | Water |

This equation represents the facts which have been repeatedly verified by experiment. The chemical change in which an acid and a base neutralize each other and form a salt and water is called **neutralization**. Taking this equation as a type of the chemical change which occurs in neutralization,

it is clear that (1) the metal of the base takes the place of the hydrogen of the acid, thereby forming a salt, while (2) the hydrogen of the acid combines with the hydrogen and oxygen of the base to form water. In neutralization the hydrogen and oxygen of the base act as a unit. This group of atoms (OH), as already stated, is called hydroxyl. Hydroxyl does not exist free and uncombined like elements and compounds, but it acts like a single atom in many chemical changes. It is called a **radical.**

Neutralization illustrates double decomposition. In the chemical change just cited both the hydrochloric acid and the sodium hydroxide are decomposed and their parts are recombined in a different way; *i.e.* sodium chloride and water are the new compounds resulting from the recombination.

Neutralization when interpreted by the theory of electrolytic dissociation is really the union of hydrogen ions with hydroxyl ions. Suppose solutions of hydrochloric acid and sodium hydroxide are mixed in the proper proportions. The mixture at first contains ions of hydrogen, chlorine, sodium, and hydroxyl. But the ions of hydrogen and of hydroxyl immediately unite to form molecules of water, because water does not dissociate into ions to any appreciable extent. The final solution is neutral, because it contains only ions of sodium and chlorine, the acid ions ($H^+$) and the basic ions ($OH^-$) having been removed by their combination into molecules of water. The equation for the mutual neutralization of hydrochloric acid and sodium hydroxide might be written as an **ionic equation**, thus: —

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Cl^- + Na^+ + H_2O$$

The ionic equations for the mutual neutralization of other pairs of acids and bases are similarly written. In the case just described, the ions of sodium and of chlorine remain uncombined until the solution is evaporated; but as the con-

centration increases, the ions unite and form molecules of sodium chloride. The latter, as already stated, is one type of the varied class of compounds called salts. The salts resulting from the combination of ions can be obtained as solids by the usual processes of evaporation to dryness or by crystallization. It is evident, therefore, that neutralization in a broad sense is the mutual destruction of an acid and a base which results in the formation of a salt and water. In a narrow sense it is the formation of molecules of water from the hydrogen ions of the acid and the hydroxyl ions of the base. This latter interpretation is supported by experimental evidence. Heat is liberated when these ions unite to form water. If neutralization is merely the combination of ions of hydrogen with ions of hydroxyl, then the same amount of heat should be liberated when a given weight of water is formed, whether the ions come from hydrochloric acid and sodium hydroxide or from any other pair of acid and base. Experiment shows that the **heat of neutralization,** as it is called, is the same in all cases of neutralization, when the solutions are dilute and other thermal changes do not occur. It is expressed in terms of a unit called the calorie, and when 18 gm. of water are formed by the act of neutralization, 13,700 calories are liberated. (See Calorie, Chapter XI.)

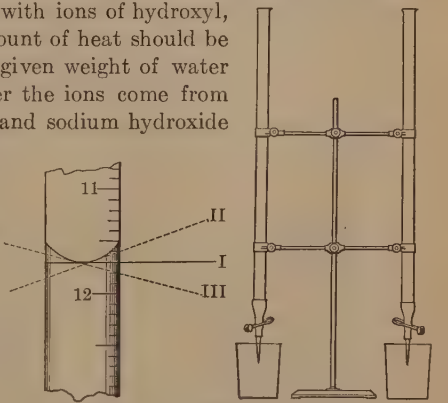



FIG. 18. — Burettes. Enlarged section (on the left) shows graduations and curved surface of the solution, called the meniscus. Correct reading is along line I.

Neutralization is frequently brought about by using burettes (Fig. 18). These are graduated tubes provided with a stopcock to regulate the exit of the solution. When properly filled, one with an acid (*e.g.* sulphuric) and the other with a base (*e.g.* sodium hydroxide), a measured volume of the acid is allowed to flow into a beaker and a few drops of litmus solution are added. The solution of course turns red. The sodium hydroxide solution is allowed to drop in slowly and the mixture is stirred with a glass rod. As long as an excess of acid is present, the color remains red. After a time, however, the color becomes purple, and an additional drop of sodium hydroxide turns the solution blue, showing that the acid has been neutralized by the base. The volume of sodium hydroxide used is noted. If solutions of known strength are used, then the weights (found from the concentration of the solutions) used will be in the same ratio as the weights in the equation: —

$$\underset{\substack{\text{Sulphuric}\\\text{Acid}\\98}}{H_2SO_4} + 2\ \underset{\substack{\text{Sodium}\\\text{Hydroxide}\\80}}{NaOH} = \underset{\substack{\text{Sodium}\\\text{Sulphate}\\142}}{Na_2SO_4} + 2\ \underset{\substack{\text{Water}\\36}}{H_2O}$$

If the concentration of the sodium hydroxide solution is unknown, it can be found by the proper proportion, because the weights involved in the chemical change are always in the ratio given in the corresponding equation. Neutralization when conducted by means of accurate apparatus and certain solutions of known strength is an efficient method of quantitative analysis and is one of a class called volumetric methods.

**Classification of Salts.** — It will be recalled that salts have no distinctive class property like acids and bases, such as the taste and behavior with litmus. From the standpoint of the chemical change which occurs in complete neutral-

ization and in analogous cases where the chemical change is not complete, a salt is a compound formed (1) by the substitution of a metal for *all or part* of the hydrogen of an acid, or (2) by the substitution of a non-metal (or non-metallic group like $SO_4$ or $NO_3$) for *all or some* of the hydroxyl groups of a base. There are, therefore, three classes of salts, — normal, acid, and basic. They are formed in various ways, but it is convenient to regard them as having been produced from an acid or a base by substitution. Salts in which all the hydrogen atoms have been replaced by a metal are called **normal salts**, *e.g.* sodium sulphate, $Na_2SO_4$. If not all of the hydrogen atoms have been replaced by the correct number of atoms of a metal, an **acid salt** is formed. Thus, acid sodium sulphate may be regarded as derived from sulphuric acid by replacing only one of the atoms of hydrogen by one atom of sodium, though of course the salt is not prepared in this way. Expressed as formulas these relations can be written thus: —

| Acid | Acid Salt | Normal Salt |
|---|---|---|
| $H_2SO_4$ | $HNaSO_4$ | $Na_2SO_4$ |

Only the acids containing two or more replaceable atoms of hydrogen can, as a rule, form acid salts; *e.g.* sulphuric acid ($H_2SO_4$) and phosphoric acid ($H_3PO_4$). An examination of the formulas of acids shows that all do not contain the same number of hydrogen atoms. Acids are sometimes classified by the number of their hydrogen atoms which can be replaced by a metal. This varying power of replaceability is called **basicity.** A **monobasic acid** contains only one atom of replaceable hydrogen in a molecule; *e.g.* nitric acid, $HNO_3$. A molecule of acetic acid ($C_2H_4O_2$) contains four atoms of hydrogen, but for reasons which are too complex to state here, only one of these atoms can be replaced by a metal; it is therefore monobasic. **Dibasic**

and **tribasic acids** contain respectively two and three replaceable hydrogen atoms; *e.g.* sulphuric acid ($H_2SO_4$) and phosphoric acid ($H_3PO_4$). Ordinarily, monobasic acids form only one class of salts, dibasic acids form two classes, tribasic acids form three, and so on. Normal salts may also be regarded as formed by the replacement of all the hydroxyl groups of a base by non-metallic atoms or atomic groups. Thus, bismuth nitrate ($Bi(NO_3)_3$) is a normal salt and may be regarded as formed by the substitution of three $NO_3$-groups for the three hydroxyl groups in bismuth hydroxide ($Bi(OH)_3$). But basic bismuth nitrate may be regarded as formed by the substitution of one $NO_3$-group for one of the three OH-groups in bismuth hydroxide. The following equation illustrates the formation of this basic salt: —

$$\underset{\text{Bismuth Hydroxide}}{Bi(OH)_3} + \underset{\text{Nitric Acid}}{HNO_3} = \underset{\text{Basic Bismuth Nitrate}}{Bi(OH)_2\,NO_3} + \underset{\text{Water}}{H_2O}$$

Not all bases contain the same number of replaceable hydroxyl groups. Hence bases, like acids, are classified according to their varying power of replaceability. This power is called **acidity.** Bases are called **monacid, diacid, triacid** bases, etc., according to the number of the replaceable hydroxyl groups present in a molecule. Thus, sodium hydroxide (NaOH) is a monacid base, calcium hydroxide ($Ca(OH)_2$) is a diacid base, and aluminium hydroxide ($Al(OH)_3$) is a triacid base. Only these bases having two or more replaceable hydroxyl groups can form basic salts, as a rule. Some basic salts have a very complex composition, and are almost insoluble in water.

**Preparation of Salts.** — It must not be concluded from the foregoing discussion of the kinds of salts that they are always prepared in the laboratory by mixing acids with bases or metals. It is only necessary to provide the metallic

or non-metallic constituent chemically, so to speak. Salts can be prepared in several ways. The interaction of an acid and a base has been mentioned. The interaction of acids with oxides of certain metals produces salts. Sodium oxide and sulphuric acid interact and form the salt sodium sulphate, thus: —

$$\underset{\text{Sodium Oxide}}{Na_2O} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Water}}{H_2O}$$

A metal and an acid act similarly. Zinc and sulphuric acid, as already stated, form the salt zinc sulphate, thus: —

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Zinc Sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{2\,H}$$

Carbonates interact with acids and form other salts. Calcium carbonate and hydrochloric acid form the salt calcium chloride, thus: —

$$\underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Hydrochloric Acid}}{2\,HCl} = \underset{\text{Calcium Chloride}}{CaCl_2} + \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Water}}{H_2O}$$

Sometimes two salts interact in solution and form other salts by double decomposition. Sodium chloride and silver nitrate form the salts silver chloride and sodium nitrate, thus: —

$$\underset{\text{Sodium Chloride}}{NaCl} + \underset{\text{Silver Nitrate}}{AgNO_3} = \underset{\text{Silver Chloride}}{AgCl} + \underset{\text{Sodium Nitrate}}{NaNO_3}$$

Salts interact with certain acids and form salts and other acids. Sodium chloride and sulphuric acid form hydrochloric acid and the salt sodium sulphate, thus: —

$$\underset{\text{Sodium Chloride}}{2\,NaCl} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Hydrochloric Acid}}{2\,HCl} + \underset{\text{Sodium Sulphate}}{Na_2SO_4}$$

**Nomenclature of Acids.** — Oxygen is a component of most acids, and the names of these acids correspond to the proportion of oxygen which they contain. The best known acid of an element usually has the suffix *-ic; e.g.* sulphuric ($H_2SO_4$), nitric ($HNO_3$), phosphoric ($H_3PO_4$). If an element forms another acid, containing less oxygen, this acid has the suffix *-ous; e.g.* sulphurous ($H_2SO_3$), nitrous ($HNO_2$), phosphorous ($H_3PO_3$). Some elements form an acid containing less oxygen than the -ous acid; these acids retain the suffix *-ous*, and have in addition the prefix *hypo-; e.g.* hyposulphurous ($HSO_2$), hypophosphorous ($H_3PO_2$), hypochlorous (HClO). *Hypo-* means under or lesser. If an element forms an acid containing more oxygen than the -ic acid, such an acid retains the suffix *-ic*, and has in addition the prefix *per-; e.g.* persulphuric ($H_2S_2O_8$), perchloric ($HClO_4$). The prefix *per-* means beyond or over. The few acids which contain no oxygen have the prefix *hydro-* and the suffix *-ic; e.g.* hydrochloric (HCl), hydrobromic (HBr), hydrofluoric (HF), and hydriodic (HI). It should be noticed that the suffixes *ic-* and *-ous* are not always added to the whole name of the element, but often to some modification of it.

The nomenclature of acids is well illustrated by the series of chlorine acids: —

Acids of the Element Chlorine

| Name | Formula |
|---|---|
| Hydrochloric | HCl |
| Hypochlorous | HClO |
| Chlorous | $HClO_2$ |
| Chloric | $HClO_3$ |
| Perchloric | $HClO_4$ |

Not all elements form a complete series of acids, but the nomenclature usually agrees with the above principles.

Some acids have commercial names. Thus, sulphuric acid is often called oil of vitriol, and hydrochloric acid is known as muriatic acid. Acids in which carbon is an essential constituent end in *-ic*, but they are often arbitrarily named. (See Organic Acids.)

**Nomenclature of Bases.** — There is no general rule for the nomenclature of bases, as in the case of acids. Since most bases contain hydrogen and oxygen, they are called **hydroxides.** The term *hydrate* is sometimes used as a synonym of hydroxide, but it more correctly describes those compounds in which water is one constituent. Thus, crystallized salts containing water of crystallization are often called hydrates. The term *alkali* emphasizes general properties rather than suggests specific composition and is now applied to the very active bases such as sodium and potassium hydroxides. Hydroxides are distinguished from each other by placing the name of the metal before the word *hydroxide; e.g.* sodium hydroxide, potassium hydroxide, calcium hydroxide.

The common hydroxides have long been known by special names. Thus, a solution of calcium hydroxide is sometimes called limewater. Ammonium hydroxide solution is sometimes called ammonia water or simply ammonia, and it was formerly called volatile alkali. The hydroxides of sodium and potassium are often called caustic soda and caustic potash, and occasionally the term *fixed alkali* is used to emphasize the fact that they are non-volatile.

**Nomenclature of Salts.** — The names of salts containing oxygen are derived from the name of the corresponding acid. The characteristic suffix of the acid is changed to indicate this relation. Thus, the suffix *-ic* becomes *-ate*, and the suffix *-ous* becomes *-ite*. Hence : —

Sulphuric acid forms sulphates.
Sulphurous acid forms sulphites.
Nitric acid forms nitrates.
Nitrous acid forms nitrites,
Chloric acid forms chlorates.
Hypochlorous acid forms hypochlorites.
Permanganic acid forms permanganates.

The name of the replacing metal is retained; *e.g.* potassium chlorate, sodium sulphate, calcium hypochlorite, potassium permanganate. Notice that the prefixes *hypo-* and *per-* are not changed.

The names of salts containing only two elements, following the general rule for binary compounds, end in *-ide*. This suffix is added to a modification of the name of the non-metal, giving the names chloride, bromide, sulphide, fluoride, etc. The prefix *hydro-* which is contained in the name of the acid is omitted. Thus, the sodium salt of hydrochloric acid is sodium chloride; similarly, there are the names potassium chloride, calcium fluoride, and sodium iodide.

**Relation of Oxides to Acids and Bases.** — Most non-metallic elements form oxides which unite with water and produce an acid. The oxides of many metallic elements, on the other hand, unite with water and produce bases. The two oxides of the non-metal sulphur act thus: —

| | | | | |
|---|---|---|---|---|
| $SO_2$ | + | $H_2O$ | = | $H_2SO_3$ |
| Sulphur Dioxide | | Water | | Sulphurous Acid |
| $SO_3$ | + | $H_2O$ | = | $H_2SO_4$ |
| Sulphur Trioxide | | Water | | Sulphuric Acid |

The oxide of the metal calcium acts thus: —

| | | | | |
|---|---|---|---|---|
| $CaO$ | + | $H_2O$ | = | $Ca(OH)_2$ |
| Calcium Oxide | | Water | | Calcium Hydroxide |

Oxides of non-metals which unite with water and produce acids are called acid forming oxides or **acid anhydrides**, *i.e.* literally, substances without water. Examples are carbonic anhydride ($CO_2$), sulphuric anhydride ($SO_3$), phosphoric anhydride ($P_2O_5$). Oxides of metals which produce basic hydroxides are base forming oxides or **basic anhydrides.** Examples are calcium oxide (CaO), sodium oxide ($Na_2O$), barium oxide (BaO). A few oxides behave exceptionally. It is convenient to regard an acid anhydride as the root or basis of its corresponding acid, and a basic anhydride as the root of its hydroxide.

The fact that many non-metallic oxides redden moist blue litmus led Lavoisier into the erroneous belief that oxygen is an essential constituent of all acids. And some authorities even now speak (incorrectly) of these oxides as acids; thus, carbon dioxide ($CO_2$) is occasionally called carbonic acid. The compounds which Lavoisier called acids were anhydrides. And it was not until about 1811 that Davy showed (1) that some acids do not contain oxygen (*e.g.* hydrochloric acid, HCl), and (2) that the so-called acids of Lavoisier are not real acids until they obtain hydrogen from the water in which they dissolve.

**Degree of Dissociation of Acids, Bases, and Salts.** — The degree to which acids, bases, and salts dissociate is due to two factors, viz. the nature of the substance itself and the concentration of the solution. In general, dissociation is slight in a concentrated solution, and increases as the solution becomes more and more dilute. Thus, in concentrated nitric acid (62 per cent) the per cent of ionized molecules is only about 9, while in a normal solution (6.3 per cent) the per cent is about 90. Similarly, in solutions of sodium chloride having decreasing concentrations in the ratio 1 : .5 : .1 the per cents of increasing dissociation are approximately 67, 73, and 84. In order to compare the varying degrees of dissociation, solutions of the same relative strength (at a fixed temperature) must be taken. Usually normal

solutions at 18° C. are selected, *i.e.* solutions which contain in a liter a number of grams numerically equal to the molecular weight divided by the number of replaceable hydrogen atoms present (or their metallic equivalent). For example, a normal solution of hydrochloric acid contains 36.5 gm. to the liter, *i.e.* $(35.5 + 1) \div 1$; but since sulphuric acid contains two replaceable hydrogen atoms, its normal solution contains $(2 + 32 + 64) \div 2 = 49$ gm. in each liter of solution. Similarly, a normal solution of sodium hydroxide contains $(23 + 16 + 1) \div 1 = 40$ gm., while one of potassium sulphate contains $(78 + 32 + 64) \div 2 = 87$ gm. to the liter of solution. Normal solutions are often designated by the letter N, and different concentrations are indicated correspondingly, *e.g.* half normal by $\frac{N}{2}$, twice normal by 2 N. The approximate per cent of dissociation of certain acids, bases, and salts is tabulated below; the solutions are one tenth normal (at 18° C.).

TABLE OF DISSOCIATION OF ACIDS, BASES, AND SALTS

| ELECTROLYTE | PER CENT OF DISSOCIATION |
|---|---|
| Nitric acid | 90 |
| Hydrochloric acid | 90 |
| Sulphuric acid | 60 |
| Acetic acid | 1.4 |
| Carbonic acid | .12 |
| Hydrocyanic acid | .01 |
| Potassium hydroxide | 86 |
| Sodium hydroxide | 86 |
| Ammonium hydroxide | 1.4 |
| Potassium chloride | 85 |
| Sodium chloride | 84 |
| Potassium nitrate | 83 |
| Potassium chlorate | 81 |
| Silver nitrate | 80 |
| Copper sulphate | 37 |

An examination of the table above shows more or less equality of dissociation among salts, but a rather wide variation in the case of both acids and bases. The term *strong* is applied to those acids and bases which dissociate to a marked degree, and the term *weak* to those whose dissociation is limited.

**Salts and the Theory of Electrolytic Dissociation.** — According to the theory of electrolytic dissociation, solutions of normal salts contain neither hydrogen nor hydroxyl ions; and, as a rule, they are neutral to litmus. But solutions of acid salts contain the ions characteristic of an acid (*i.e.* H-ions or $H^+$) as well as the ions of a salt. While solutions of basic salts contain the ions characteristic of a base (*i.e.* hydroxyl ions or $OH^-$) as well as the ions of a salt. **A salt** may be defined in terms of the theory of electrolytic dissociation as the compound ultimately formed by the union of one or more metallic ions of the base and one or more non-metallic ions of an acid, supplemented in some cases by one or more hydrogen or hydroxyl ions. In other words, salts are chemical compounds which have a certain composition but not necessarily uniform behavior. For example, take the behavior toward litmus. Normal salts are neutral, acid, or basic; acid salts are acid or nearly neutral; most basic salts are nearly insoluble in water, and exhibit a faint reaction toward litmus. The terms *normal*, *acid*, and *basic* as applied to salts indicate their composition but do not describe their properties. An explanation of this varying behavior of salts toward litmus is offered by the theory of electrolytic dissociation. Hitherto, pure water has been referred to as a non-electrolyte, and in most solutions there is no evidence of its dissociation into the ions $H^+$ and $OH^-$. In some cases, however, the very slight ionization of water becomes a significant factor in establish-

ing the properties revealed by the solution; *i.e.* its ions, though comparatively very few in number, interact with the ions of certain substances which likewise dissociate to a slight degree. Thus, sodium carbonate yields the ions $2\ Na^+$ and $CO_3^{--}$. But the $CO_3$-ions combine at once with H-ions to form the ion $HCO_3^-$ — the last named being one of the ions yielded by the slightly dissociated acid, $H_2CO_3$. The removal of H-ions leaves an excess of OH-ions, which give the solution an alkaline reaction toward litmus. On the other hand, copper sulphate (a normal salt from the standpoint of composition) has an acid reaction. It yields the ions $Cu^{++}$ and $SO_4^{--}$. But the Cu-ions combine with OH-ions to form copper hydroxide ($Cu(OH)_2$), which dissociates only to a very slight extent. The removal of OH-ions leaves an excess of H-ions in the solution and gives it an acid reaction. For similar reasons the litmus reaction of potassium carbonate and potassium cyanide is alkaline, while the reaction of ferric chloride is acid. In the case of acid salts, the explanation is of the same order. Acid sodium sulphate ($HNaSO_4$) yields the ions $Na^+$ and $HSO_4^-$, but the latter ion dissociates to some extent into $H^+$ and $SO_4^{--}$; the solution is therefore rendered acid to litmus by the H-ions. But acid sodium carbonate ($HNaCO_3$) is nearly neutral to litmus. It yields the ions $Na^+$ and $HCO_3^-$; but since the latter dissociates to only a very slight extent, the solution is not provided with an excess of either H-ions or OH-ions, and therefore has only a fairly neutral reaction. The chemical changes cited in this paragraph are examples of a general phenomenon called **hydrolysis**, *i.e.* a chemical change (double decomposition) brought about by the interaction of certain salts and water. It is typically exhibited by salts derived from strong bases (*e.g.* NaOH and KOH) and weak acids (*e.g.* $H_2CO_3$ and HCN), or from weak bases (*e.g.* $Cu(OH)_2$ and $Fe(OH)_3$) and strong acids (*e.g.* HCl and

$H_2SO_4$). The behavior of the final solution toward litmus depends upon the composition of the salt, as the following equations show. The ordinary chemical equation for the hydrolysis of sodium carbonate is —

$$\underset{\text{Sodium Carbonate}}{Na_2CO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Acid Sodium Carbonate}}{HNaCO_3} + \underset{\text{Sodium Hydroxide}}{NaOH}$$

The ionic equation is —

$$2\,Na^+ + CO_3^{-\,-} + H^+ + OH^- \rightarrow 2\,Na^+ + HCO_3^- + OH^-$$

The corresponding equations for the hydrolysis of copper sulphate are —

$$\underset{\text{Copper Sulphate}}{CuSO_4} + 2\,\underset{\text{Water}}{H_2O} = \underset{\text{Copper Hydroxide}}{Cu(OH)_2} + \underset{\text{Sulphuric Acid}}{H_2SO_4}$$

$$Cu^{++} + SO_4^{-\,-} + 2\,H^+ + 2\,OH^- \rightarrow Cu(OH)_2 + SO_4^{-\,-} + 2\,H^+$$

### Problems and Exercises

1. Name the hydroxide corresponding to sodium, potassium, calcium, barium, zinc, lead, copper.

2. Name the potassium salt of manganic acid, calcium salt of hydrofluoric acid, sodium salt of carbonic acid, potassium salt of tartaric acid, lead salt of chromic acid, potassium salt of hydrobromic acid, potassium salt of permanganic acid.

3. Name the sodium salt of hydrochloric acid. Name the corresponding salt of potassium, lead, calcium, barium, zinc, silver.

4. Name the same salts of nitric acid. Of nitrous acid.

5. Name the same salts of sulphuric acid. Of hypochlorous acid. Of perchloric acid.

6. What weight of sulphuric acid is needed to neutralize 40 gm. of potassium hydroxide?

7. The specific gravity of a solution of hydrochloric acid is 1.175 and it contains 34.4 per cent of the compound HCl. How many cubic centimeters of the solution must be taken to neutralize 60 gm. of sodium hydroxide?

8. What is the per cent of hydrogen in (*a*) sulphuric acid, (*b*) hydrochloric acid, (*c*) nitric acid?

9. What is the per cent of OH in (*a*) NaOH, (*b*) KOH, (*c*) $NH_4OH$, (*d*) $Ca(OH)_2$?

10. Write equations for the following reactions: (*a*) Hydrochloric acid neutralizes sodium hydroxide and forms sodium chloride and water. (*b*) Nitric acid neutralizes potassium hydroxide and forms potassium nitrate and water. (*c*) Potassium chloride and silver nitrate form silver chloride and potassium nitrate. (*d*) Carbon dioxide and water form carbonic acid ($H_2CO_3$). (*e*) Barium oxide and water form barium hydroxide. (*f*) Potassium carbonate by hydrolysis forms acid potassium carbonate and potassium hydroxide.

11. Write the ionic equations for (*a*) and (*b*) in Problem 10.

## CHAPTER XI

### Light, Heat, Electricity, and Chemical Change

Chemical change is always attended by the production or consumption of one or more of the different forms of energy, such as light, heat, and electricity. This means that a chemical change involves not only a rearrangement of matter, but also a transformation or redistribution of energy. Thus, when coal is burned, a new compound, called carbon dioxide, is formed, but heat is also liberated as a result of the chemical change. Sometimes we pay more attention to the redistributed matter than to the energy, but both are involved. In the present chapter we shall emphasize the relation of energy to chemical change.

The law of the conservation of energy should be recalled in this connection. Energy, like matter, cannot be created or destroyed by any known means; we can only transform it. Hence, the chemical energy that is locked up, so to speak, in elements and compounds reveals itself as heat, light, or electricity. And these common forms of energy are in turn often transformed into chemical energy and stored up in the chemical elements and compounds which are the result of chemical changes.

#### Light and Chemical Change

Light is often produced by chemical change. Sometimes the light is faint, as in the slow oxidation of yellow phosphorus, which is luminous in moist air. This phenomenon is also exhibited by mixtures containing even a very little

phosphorus; for example, the head of a sulphur match. When the phosphorus and oxygen unite, part of the energy in each element is transformed into light and part is stored up in the phosphorus pentoxide. Usually the transformation of chemical energy into light is more vivid; that is, more chemical energy becomes light. Many chemical experiments are accompanied by intense light, especially those involving combination with oxygen or with chlorine. Thus, magnesium burns in oxygen with a dazzling light, and powdered antimony, as well as some other metals, bursts into a flame when dropped into chlorine gas. Combustion in general, especially of coal, oils, and gases containing compounds of carbon, is usually attended by light, and serves as an excellent illustration of the transformation of chemical energy into light during chemical changes.

Light is also often transformed into chemical energy. This transformation is typically illustrated by photographic processes. Paper, glass plates, and films coated with compounds of silver are blackened on exposure to the light; the compounds are changed chemically and light is transformed into chemical energy. Another transformation more or less familiar is that involved in the fading of colored fabrics, wall paper, and paintings. Light is also absolutely essential in the complex chemical changes involved in the growth of plants. The sunlight is stored up in the plants and is subsequently utilized by mankind when wood and coal are burned as fuel or vegetable matter is consumed as food. Certain chemical changes which proceed very slowly are hastened by light. Thus, hydrogen and chlorine gases when mixed in the dark do not unite perceptibly, but they combine slowly in diffused light and instantaneously in the direct sunlight. Similarly, a solution of chlorine (in water) evolves oxygen slowly in the dark but more rapidly in the light.

### Heat and Chemical Change

Heat and chemical change are closely and definitely related. A chemical change is almost invariably accompanied by the liberation or absorption of heat, usually the liberation. Vigorous and rapid reactions develop considerable heat and are also often attended by light, while the heat evolved by feeble or slow reactions is comparatively slight and sometimes can scarcely be detected.

A familiar instance of the evolution of heat by chemical change is the slaking of lime. Lime is calcium oxide (CaO), and when lime and water are mixed their chemical union produces sufficient heat to boil water and often to set fire to wood. Steam can be seen escaping from the boxes in which lime is being mixed with water in the preparation of plaster or mortar. Buildings in which lime is stored sometimes take fire, if rain leaks in upon the lime. Ships loaded with lime are in constant danger of being set afire. Another illustration is provided by the combustion of fuels such as coal, wood, oils, and gases. These are largely carbon. The carbon in these substances unites with the oxygen of the air, and the chemical energy in both elements becomes heat to a great extent, some of course remaining in the products of combustion. Many chemical changes, already considered, are attended by the liberation of heat, the most conspicuous being the act of combination with oxygen. Thus, when hydrogen burns, the act of combination is strikingly manifested by the colorless, intensely hot flame. The interaction of metals and acids, as seen in the preparation of hydrogen, develops heat. The chemical union of sulphur and metals is often accompanied by heat sufficient to cause incandescence. Reduction of metallic oxides often liberates much heat. For example, the heat attending the reduction of iron oxide by aluminium is so intense that the iron melts. (See Thermit.)

Many chemical changes take place slowly at the ordinary temperature. Once started by heat, however, they proceed until the interacting substances are exhausted or the external supply of heat is removed. There are many illustrations of this hastening of chemical change by heat. Magnesium tarnishes very slowly in the air, but if a lighted match is applied to the metal, oxidation proceeds rapidly until the magnesium is entirely changed into magnesium oxide. Hydrogen and oxygen mix freely at the ordinary temperature without appreciable combination; if mixed in the proportion of two volumes to one and heated to 600° C., combination takes place in about one hour, while union instantly occurs when heat is applied in the form of a flame or an electric spark. Similarly, illuminating gas must be lighted before it will interact chemically with the oxygen of the air, but once raised to the proper temperature, the chemical change continues as long as the gas is supplied. Combustible substances, such as wood, many oils and gases, sulphur, and phosphorus, must be raised to a certain temperature called the **kindling temperature** before the chemical changes that liberate heat can proceed. The kindling temperature varies with the physical condition in the case of many solids, being lower, as a rule, when the substance is finely divided or presents a relatively large surface. Thus, shavings catch fire at a lower temperature than a stick or log of the same variety of wood. In many chemical changes heat must be constantly supplied. Thus, mercuric oxide decomposes into mercury and oxygen as long as it is sufficiently heated, but when the flame is removed, the chemical change slackens and soon ceases altogether. The same is true of potassium chlorate. Indeed, heat is one of the most efficient aids to chemical change, and various sources of heat are indispensable in the laboratory as well as in chemical manufactories.

**Sources of Heat.** — Heat is so essential in all chemical operations that chemists have devised and used many appliances for generating intense and continuous heat. The alchemists burned wood and charcoal in the furnaces which heated their crucibles. Priestley and Lavoisier employed a lens or burning glass in some of their experiments. Liebig and his contemporaries used a charcoal furnace in analyzing organic compounds. The greatest advance was made when Bunsen invented the burner which consumes gas and produces a hot, smokeless flame. This burner is replaced by the blast lamp and oxyhydrogen blowpipe whenever a very high temperature is desired (see Figs. 4 and 5). In the arts and industries various kinds of furnaces are used; *e.g.* reverberatory, open hearth, and blast (see Figs. 64, 82, and 80). But all these sources of heat have been surpassed by the electric furnace. It is well known that an electric arc light produces intense heat. The high temperature of the arc, *i.e.* space between the glowing ends of the carbons, is unequaled by that of any other source of artificial heat. If the carbon rods are inclosed in an infusible box or vessel that prevents escape of heat, a temperature estimated to be about 3500° C. can be produced inside the receptacle. This apparatus is called an electric furnace. One form of the electric furnace is shown in Figure 19. When a current is passed through the carbon rods, the tremendous heat produced within the space is retained by the nonconducting walls and acts upon the substance in the crucible below the arc. The outside of the furnace remains cold enough to be touched by the hand, but the inside

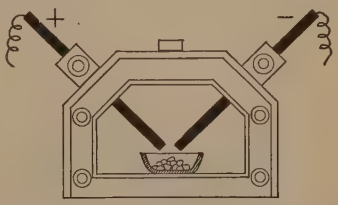


FIG. 19. — Electric furnace — arc type.

is almost twice as hot as the oxyhydrogen flame. There is no electrical action upon the chemicals. The intense heat alone produces the remarkable physical and chemical changes, and for this reason the process is often called an electrothermal process. Sand, lime, magnesium oxide, and other refractory substances melt and volatilize. The elements carbon, silicon, and boron boil; and gold, copper, and platinum quickly melt and vaporize. Large masses of rare and uncommon elements are quickly reduced from their oxides and obtained in the pure state; *e.g.* chromium, manganese, tungsten, uranium, and molybdenum. Stable compounds of carbon, boron, and silicon are formed. These are the carbides, borides, and silicides. Some of the carbides have an industrial use as well as scientific interest, especially calcium carbide and silicon carbide.

Another form of electric furnace is shown in Figure 20. In this kind the substance itself helps generate heat, for the

FIG. 20. — Electric furnace — resistance type.

current in passing between the ends of the electrodes, as the carbon rods are called, meets with so much resistance that intense heat is produced. Large electric furnaces constructed on this type are now in practical operation. And since electricity is obtained in many localities by operating dynamos by water, new industries requiring intense and continuous heat have recently sprung into existence and older ones have been remodeled. Some of these plants are

located at Niagara Falls, which furnishes enormous power at a relatively small expense. Several commercial substances, more or less familiar, are manufactured in the electric furnace; *e.g.* calcium carbide, carborundum, alundum, phosphorus, carbon disulphide, graphite, and silicon. These are discussed in appropriate places.

**Measurement of Heat Energy.** — Every substance possesses a certain amount of chemical energy, but there is no way of determining the exact amount. We can, however, measure that part of the chemical energy which is transformed into heat when a substance or set of substances undergoes a chemical change. Thus, when hydrogen and oxygen combine chemically, the total amount of chemical energy in the two gases is divided, part being liberated as heat, and part being locked up as chemical energy in the water. The liberated heat may be taken as a rough measure of the chemical energy transformed during the chemical change. The experiment is performed in a calorimeter. This apparatus consists essentially of two parts, a small vessel in which the substance is chemically changed and a larger one containing water in which the small vessel is immersed. The heat liberated by the chemical change raises the temperature of the water. Heat is measured in calories, a calorie being the quantity of heat necessary to raise 1 gm. of water 1° C. in temperature (provided the degree is between 0° and 100° C.). For example, the heat liberated by the burning of 1 gm. of hydrogen is 34,200 cal. Attention has already been called to the high temperature of the hydrogen flame. (See Chapter III.)

Ordinary chemical equations do not express changes in energy. To represent heat changes, the number of calories of heat involved is placed after the equation, together with the proper sign, thus: —

$$\underset{\substack{\text{Hydrogen}\\2}}{2H} + \underset{\substack{\text{Oxygen}\\16}}{O} = \underset{\substack{\text{Water}\\18}}{H_2O} + 68{,}400 \text{ cal.}$$

This is called a **thermal equation**, and it means that 68,400 cal. of heat are liberated when 2 gm. of hydrogen unite with 16 gm. of oxygen to form 18 gm. of water. In some chemical changes heat is absorbed. Thus, when carbon unites with sulphur to form carbon disulphide, heat is absorbed. The equation expressing this fact is —

$$\underset{\substack{\text{Carbon}\\12}}{C} + \underset{\substack{\text{Sulphur}\\64}}{S_2} = \underset{\substack{\text{Carbon Disulphide}\\76}}{CS_2} - 19{,}600 \text{ cal.}$$

Heat involved in the formation of a particular compound is called heat of formation of that compound. If heat is liberated in the formation of a compound, the heat is designated positive (+); and the compound is termed **exothermic**. Heat of formation which is absorbed is designated negative (−); and a compound having a negative heat of formation is said to be **endothermic**. Exothermic compounds are relatively stable; they can be decomposed by the addition of the same quantity of heat liberated by their formation. Thus, 68,400 cal. of heat or an equivalent quantity of energy must be added to 18 gm. of water to decompose it into 2 gm. of hydrogen and 16 gm. of oxygen. Such heat is called heat of decomposition. On the other hand, endothermic compounds are unstable and often explosive. They decompose easily with the liberation of heat. Ozone is endothermic. Heat is absorbed during its formation from oxygen, but when ozone decomposes, heat is liberated. Two parts (by volume) of ozone form 3 parts (by volume) of oxygen and liberate 72,400 cal. Acetylene is also endothermic. (See Acetylene.) In the preceding chapter attention was called to the fact that the interaction of equivalent quantities of

strong acids and bases liberates the same quantity of heat; that is, the heat of neutralization liberated by the union of hydrogen and hydroxyl ions is 13,700 cal. under normal conditions. The thermal equation for the neutralization of sodium hydroxide by hydrochloric acid is —

$$NaOH + HCl = NaCl + H_2O + 13{,}700 \text{ cal.}$$

Applications and extensions of thermochemistry, as this branch of the science is called, will be made in subsequent chapters.

### Electricity and Chemical Change

**The Relation between Electricity and Chemical Action** has always been a fascinating subject. Volta constructed his voltaic pile about 1800. This was one of the first (perhaps the first) sources of an electric current. In May, 1800, Nicholson and Carlisle decomposed water into hydrogen and oxygen by an electric current obtained from a thermopile. In the same year Cruikshank obtained lead and copper from solutions of their salts. And in 1807 Davy isolated two elements, sodium and potassium, by passing an electric current (obtained from a large battery) through fused sodium hydroxide and potassium hydroxide respectively. From that time until the present day the relation between electricity and chemical change has engaged the attention of chemists, and their labors have built up a branch of chemistry called electrochemistry, which has recently attained considerable commercial importance.

**Transformations of Electrical and Chemical Energy.** — Electricity, like heat and light, is readily transformed into chemical energy, and *vice versa*. Certain chemical changes produce electricity, while electricity is consumed in others.

A typical illustration of the transformation of chemical

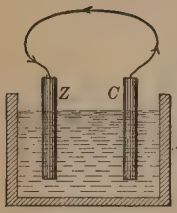



FIG. 21. — Simple voltaic cell.

energy into electricity is furnished by the **voltaic cell.** The simplest form consists of two unlike metals, such as copper and zinc, connected by a wire and partly immersed in a vessel containing dilute sulphuric acid (Fig. 21). When the connected metals are put into the acid, the zinc slowly disappears and hydrogen bubbles appear on the copper. Further examination shows that zinc sulphate is also formed. The chemical change is essentially the one already described under hydrogen, and can be represented thus : —

$$\underset{\text{Zinc}}{Zn} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{H_2SO_4} = \underset{\text{Hydrogen}}{2H} + \underset{\substack{\text{Zinc}\\\text{Sulphate}}}{ZnSO_4}$$

The wire becomes electrified and exhibits the effects of an electric current. For example, it becomes warm and makes a magnetic needle move. The source of the electric current is the chemical action between the acid and zinc. The copper is necessary, otherwise the product of the chemical action would be merely heat. Carbon is often used instead of copper, and sulphuric is replaced by other liquids, such as solutions of ammonium chloride or potassium hydroxide. The liquid chosen, however, must be one that will interact with zinc or its substitute. The zinc is ultimately transformed into zinc sulphate or some other chemical compound, and must be replenished; the solution must likewise be renewed. This necessity of recharging the cell is a striking proof of the intimate relation between chemical change and electricity. Several cells joined together form an electric battery. For many years the battery was the chief source of the electric current; and it is now widely used to generate the currents of moderate intensity utilized in ringing bells

and operating electrical apparatus. Powerful currents, as a rule, are obtained from a dynamo.

The transformation of electricity into chemical energy is illustrated by electrolysis. In Chapter IX considerable space was devoted to a discussion of the electrolysis of solutions; *i.e.* to the chemical changes which accompany the passage of an electric current through a solution. But electrolysis is not limited to solutions. Fused (*i.e.* melted) substances also undergo chemical changes when subjected to the action of a powerful electric current. As already stated, electrolysis is accomplished in an **electrolytic cell.** This apparatus differs from a voltaic cell in one essential respect. The voltaic cell produces electricity, whereas the electrolytic cell consumes electricity. Otherwise both have three main parts, — the containing vessel, two electrodes, and the electrolytic solution or fused electrolyte. A simple electrolytic cell is shown in Figure 22. In such a cell the current from the battery or dynamo enters the cell through the positive (+) electrode or anode and leaves through the negative (−) electrode or cathode. Electrodes may be of platinum, copper, zinc, mercury, or hardened carbon; they may have any shape, — rod, wire, sheet, plate, box, crucible; and they also may be solid, liquid, or powder, as well as fixed or movable. The electrodes are connected by wires with the source of the electric current, and serve as "doors" — to quote Faraday — for the current to flow into and out of electrolytic solution or the electrolyte. We speak of a "current" of electricity and of electricity as "flowing," although we do not know the fundamental nature of elec-

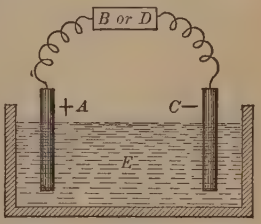



FIG. 22. — Simple electrolytic cell.

tricity nor do we mean really that it flows, like a river, only in one direction. The anode is the electrode that is often consumed or worn away, either mechanically or chemically, but solids, especially metals, are often deposited upon the cathode. The containing vessel likewise may have any desired shape, and is usually made of some material which will resist the corrosive action of chemicals; *e.g.* porcelain, slate, or soapstone. Metallic vessels lined with various substances selected to withstand intense heat are also used, since fused electrolytes are often subjected to electrolysis.

The phenomena exhibited during the electrolysis of solutions have been described. (See Chapter IX.) Certain features of the operation, however, should be recalled at this point, since they apply to both fused and dissolved electrolytes. Employing the interpretation offered by the theory of electrolytic dissociation, the ions of the electrolyte begin to migrate as soon as the electric current enters the cell; the electro-negative anions move toward the electro-positive anode, and the electro-positive cations move toward the electro-negative cathode. Reaching their respective electrodes, the ions give up their charges and become atoms, atomic groups, or molecules. The discharged particles may escape as gases, dissolve in the liquid, or attach themselves to the electrodes; very often secondary chemical changes occur which complicate the process and sometimes cause serious difficulties in industrial applications of electrolysis.

A third illustration of the transformation of electrical energy into chemical energy, and *vice versa*, is furnished by the storage cell. This cell consists essentially of two grids of lead which are filled with a mixture of sulphuric acid and lead oxide (PbO) and then immersed in a vessel containing dilute sulphuric acid. The mixture in the grids soon becomes lead sulphate ($PbSO_4$). When an electric current is passed through the cell from one plate to the other, the

hydrogen ions formed by the ionization of the sulphuric acid migrate to the cathode, where they become atomic hydrogen and by their chemical interaction with the lead sulphate form sulphuric acid and metallic lead — the latter remaining attached to the grid (cathode); the $SO_4$-ions migrate to the anode, where they become ordinary uncharged atomic groups and by their interaction with the lead sulphate form sulphuric acid and lead dioxide ($PbO_2$) — the latter remaining attached to the grid (anode). These changes continue until nearly all the lead sulphate has been altered as just described. If, after being charged, the grids are connected by a wire, a current of electricity will be obtained in a direction opposite to that used in charging the cell, and the chemical changes will take place in the reverse direction. The cell gradually reverts to its original condition, and must be recharged if a current is again desired. In this cell, therefore, there is a complete circuit of transformation, — electricity → chemical energy → electricity.

**Industrial Applications of Electrolysis.** — The earliest industrial application of electrolysis was in electrotyping and electroplating. These operations consist in depositing a thin film of metal upon a surface. They are fundamentally the same, though copper is the only metal used for producing electrotypes. Electrotypes are exact reproductions of the original object. The process of **electrotyping** is substantially as follows: The page of type, for example, is first reproduced in wax. This exact impression is next covered with powdered graphite to make it conduct electricity. The coated mold is then suspended as the cathode in an acid solution of copper sulphate; the anode is a plate or bar of copper. When the current is passed through the system, electrolysis occurs; copper is dissolved from the anode and

deposited on the mold in a film of any desired thickness. The exact copper copy is stripped from the mold, backed with metal, and used instead of the type itself. By this process, exact copies of expensive wood engravings can be cheaply reproduced and type can be saved from the wear and tear of printing. Most books, magazines, and newspapers are now printed from electrotypes. The process of **electroplating** differs from electrotyping in only one essential; viz. in electroplating the deposited film is not removed from the object. The object to be plated is carefully cleaned and made the cathode; the anode is a bar or plate of the metal to be deposited. When the current passes through the system, the metal is firmly deposited on the object. The electrolysis would take place, of course, if any anode were present; but anodes of the metal to be deposited are usually used to prevent the solution or "bath" from weakening. They accomplish the purpose by replenishing the solution with metal as fast as it is removed and deposited upon the cathode. Silver, nickel, and gold are the usual metals used in electroplating. (See these metals.)

Electroplating and electrotyping have been done since about 1840. It is only within the last ten or fifteen years, however, that the electric current has been profitably applied in many industries. But during this time the development of electrochemistry has been very marked. The largest of these industries is the refining of copper. The process is similar to that described under electrotyping. Other metals, such as gold, silver, and lead, are extracted from their ores and purified by electricity, though the older processes are still used. The aluminium, magnesium, and sodium of commerce are now manufactured by passing an electric current through their fused compounds. Chlorine, potassium chlorate, potassium hydroxide, and sodium hydroxide are some of the other important industrial products of

electrolysis. These electrochemical processes and products will be fully discussed in the appropriate places.

**Measurement of Electrical Energy.** — Faraday was the first scientist to make a thorough study of electrolysis. He found that a given current of electricity liberated different but definite amounts of the chemical elements. Thus, the current which liberates 1 gm. of hydrogen also liberates 8 gm. of oxygen, 35.46 gm. of chlorine, 107.88 gm. of silver, 31.78 gm. of copper, and so on. These numbers are identical with the chemical equivalents of these elements. (Compare Equivalents, Chapter XIV.) Faraday called them electrochemical equivalents, to emphasize their chemical and electrical relationship. But the term *electrochemical equivalent* now means the weight of an element deposited or liberated by a specified current in a certain time (1 ampere in 1 second). For example, the electrochemical equivalent of hydrogen is .000010441 gm., of oxygen is .00008287 and sometimes .00016574, of copper is .0003294 and sometimes 0.0006588, of silver is .001118. This general relation is often stated as **Faraday's law**, thus: —

*When the same current of electricity is passed through solutions of different electrolytes, the ratio of the quantities of liberated products is the same as that of their chemical equivalents.*

Faraday also showed that —

*The amount of decomposition — the chemical work, we might say — is proportional to the total amount of electricity used.* It makes no difference whether the current is strong or weak, nor whether the time of its flow is long or short. A certain quantity of electricity will do so much chemical work — no more and no less. Thus, a given quantity of electricity passed through copper sulphate solution always deposits the same weight of copper at the cathode.

These two principles of Faraday are at the foundation of all electrochemical industries. Their importance can hardly be overestimated.

### Other Conditions affecting Chemical Action

Substances vary in their tendency to undergo chemical change. Some, like oxygen, are active elements; *i.e.* they unite directly with other substances, liberate energy rapidly, and form comparatively stable compounds. Others, like nitrogen, are inert, and form relatively stable compounds by indirect processes. Not only does the chemical activity of substances differ, but the same substance is not equally active toward all others. Thus, iron unites readily with sulphur and bromine, but not with copper or mercury. Nevertheless, certain substances which are inert under ordinary conditions become active under special conditions. That is, chemical action depends not only upon the interacting substances, but also upon the specific conditions under which the reaction occurs. Chemical changes which take place so slowly as to be scarcely detected sometimes proceed with astonishing rapidity under the influence of heat, light, or electricity. Numerous illustrations have already been given of the rôle played by the different forms of energy in chemical change. In many chemical changes, however, the determining factor is not one of the familiar forms of energy, but solution, catalysis, or equilibrium.

**The Effect of Solution** on chemical change was discussed in Chapter IX. The facts recorded there need not be repeated, but certain salient conclusions should be recalled. For example, many chemical changes are carried out in aqueous solutions solely because many dissolved substances are in a condition especially suited for interaction. Indeed, substances which interact at all will usually do so in solu-

tion. "Wet processes," as they are sometimes called, are exceedingly important in chemical analysis. Again, it is found by experiment that the velocity with which the reaction proceeds is influenced by the concentration of the solutions. If the concentration of either solution is increased, the reaction takes place more rapidly; that is, in general, the greater the concentration, the greater the reaction velocity. A concrete illustration will make this point clearer. An acid solution of potassium iodide and starch turns blue when an oxidizing agent is added, owing to the interaction of the starch and the liberated iodine. If the potassium iodide solution and oxidizing solution are added to the same volume of water, the time required to produce a standard blue color will be a relative measure of the reaction velocity. The following table shows the result of an experiment: —

Measurement of Reaction Velocity

| Solution | Oxidizing Solution | Potassium Iodide Solution (cc.) | Time in Minutes |
|---|---|---|---|
| I | 5 | 5 | 4 |
| II | 10 | 5 | 2 |
| III | 5 | 10 | 2 |
| IV | 10 | 10 | 1 |

From the table it is evident that as the concentration of solution IV is four times that of solution I, the time for IV is one fourth that of I; solutions II and III have the same concentration and their times are the same.

**Catalysis.** — Slow chemical changes can often be hastened by the presence of certain substances that apparently do not participate in the chemical change and can be recovered without loss after the action has ceased. Such substances are called **catalytic agents** or **catalyzers**, and their influence

upon chemical action is called **catalysis** or **catalytic action.** For instance, potassium chlorate yields oxygen slowly when heated to about 350° C., but if powdered manganese dioxide is added, the gas is evolved rapidly. Furthermore, the manganese dioxide can be recovered after the experiment merely by dissolving out the residual potassium chloride.

Similarly, hydrogen dioxide ($H_2O_2$) decomposes very slowly in the air, but if manganese dioxide is added, the decomposition proceeds rapidly and bubbles of oxygen gas can be seen rising through the liquid. Likewise, a mixture of hydrogen and oxygen at the ordinary temperature reveals no tendency toward chemical action, but if a little powdered platinum is added, the gases combine with almost explosive violence. Again, sulphur dioxide gas ($SO_2$) and oxygen unite very slowly indeed, but when a purified and cooled mixture of these gases is passed over finely divided platinum, the gases unite rapidly and form sulphur trioxide ($SO_3$). This rapid transformation is utilized in one process of manufacturing sulphuric acid. Water vapor in traces is regarded by some authorities as a catalytic agent. Thus, many gases, especially hydrogen chloride (HCl) and ammonia ($NH_3$), do not unite when perfectly dry, but if a trace of water is added, the reaction proceeds as ordinarily observed; *i.e.* white fumes of ammonium chloride ($NH_4Cl$) are formed.

In all these accelerated chemical changes, the catalyzer probably does not react chemically with the other substance, but serves merely as an aid to the chemical change, somewhat as oil facilitates the movement of machinery. Catalysis is doubtless more important than was formerly realized, and is still under investigation.

**Reversible Reactions and Chemical Equilibrium.** — Hitherto we have described chemical reactions as if they proceeded to completion. Indeed, they do apparently, for in many

experiments conditions are chosen which necessitate action until one or more of the interacting substances is exhausted. As a matter of fact many reactions are reversible; that is, they proceed in one direction under one set of conditions and in the opposite direction under another set of conditions. For example, in the manufacture of oxygen from barium oxide a reversible reaction occurs. When barium oxide is heated in the air to about 700° C., the chemical change is represented thus: —

$$\underset{\text{Barium Oxide}}{BaO} + \underset{\text{Oxygen}}{O} = \underset{\text{Barium Dioxide}}{BaO_2}$$

If the air supply is cut off and the pressure (in the retorts) is reduced, the chemical change is reversed and may be represented thus: —

$$\underset{\text{Barium Dioxide}}{BaO_2} = \underset{\text{Oxygen}}{O} + \underset{\text{Barium Oxide}}{BaO}$$

Another illustration is provided by Lavoisier's famous experiment described under Hydrogen (see Chapter III). He passed steam over red-hot iron and obtained hydrogen and iron oxide; the equation for the chemical change is —

$$\underset{\text{Water}}{4\,H_2O} + \underset{\text{Iron}}{3\,Fe} = \underset{\text{Hydrogen}}{8\,H} + \underset{\text{Iron Oxide}}{Fe_3O_4}$$

When hydrogen is passed over hot iron oxide, the chemical change is reversed, thus: —

$$\underset{\text{Hydrogen}}{8\,H} + \underset{\text{Iron Oxide}}{Fe_3O_4} = \underset{\text{Iron}}{3\,Fe} + \underset{\text{Water}}{4\,H_2O}$$

We might conclude that in reversible reaction the chemical change may proceed in either direction to completion. As a matter of fact the actual or effective chemical change depends upon the conditions. Thus, in the interaction of

steam and iron, if the hydrogen is continuously swept out of the tube by the steam, no reduction of the iron oxide occurs; or if in the interaction of hydrogen and iron oxide the steam is continuously removed, no oxidation of iron will occur. But when the experiment is performed in a closed tube, the result is an equilibrium between these two opposing tendencies. Not only does the interaction of the steam and iron produce hydrogen and iron oxide, but conversely, the interaction of the hydrogen and iron oxide forms steam and iron. The reactions proceed simultaneously in the same tube until chemical equilibrium is reached; that is, not to completion in either direction, but in both directions until there is no further alteration in the relative weights of the substances participating in the total chemical change. Let us illustrate more definitely. If iron and steam are heated in a closed tube, the weight of steam gradually decreases and the weight of hydrogen increases until no further chemical change is apparent, even though iron and iron oxide are present; conversely, if hydrogen and iron oxide are heated in a closed tube, the weight of hydrogen gradually decreases and the weight of steam increases to a certain point, and then the chemical change apparently ceases. In each tube the ratio of the weight of hydrogen to that of steam is the same, that is, these two gases are in equilibrium. (To simplify the illustration, we confine our attention to the gases.) In general, both reactions, the direct and reverse, do not proceed until the reacting substances are completely transformed, but only to a point such that all the participating substances are in a state of chemical equilibrium. Chemical action does not cease. In equilibrium both direct and reverse reactions are still taking place, but the further accumulation of any one of the products has ceased. The system is in kinetic repose, so to speak; it is balanced rather than stopped.

Reversible reactions, then, are chemical reactions which tend to proceed until chemical equilibrium is established. They are sometimes called incomplete reactions because they cease before one or more of the interacting substances is completely transformed. In representing reversible reactions where equilibrium is finally reached, it is customary to replace the sign of equality used in the ordinary equation by oppositely directed arrows, thus: —

$$BaO + O \rightleftarrows BaO_2$$

$$4\,H_2O + 3\,Fe \rightleftarrows 8\,H + Fe_3O_4$$

The arrows emphasize the reversible character of the reaction, and the equation may be read in either direction. Like all equations, however, reversible equations tell only a partial story. Thus, neither reaction reaches completion, and the reversible equation really shows what reactions would take place provided they did not interfere. Again, a reversible equation does not show the proportion of the interacting substances actually transformed when equilibrium is reached. That is, it is not an equation in the strict sense, because the total weight on each side is not the same. Thus, if weights of hydrogen and iodine proportional to their molecular weights are heated in a closed tube to 445° C., a reversible reaction occurs. When equilibrium is reached, the tube contains 21 per cent of hydrogen and iodine and 79 per cent of hydrogen iodide (HI). The reversible equation is —

$$2\,H + 2\,I \rightleftarrows 2\,HI$$

Substituting the atomic weights, the equation becomes —

$$2 + 254 = 256$$

But the actual weights are —

$$.21\ (2 + 254) = .79\ (256)$$

— clearly an incorrect equation from a mathematical standpoint. Nevertheless, when reversible equations are interpreted in the light of the facts connected with the total reaction, they are serviceable.

Several illustrations of physical equilibrium have already been given. For example, in discussing saturated solutions (see Chapter V) it was pointed out that such solutions are readily interpreted, if we regard the solute and solvent as in equilibrium; that is, not at a standstill, but so related that in a given time the same amount of solute passes into and out of the solution. Another instance was the relation between water vapor and water where gases are confined in tubes over water. Here the particles of vapor try to fly back into the water, and the water particles try to escape as vapor; the processes reach equilibrium at a point determined by temperature and atmospheric pressure. States of equilibrium are sometimes reached in the case of efflorescent and deliquescent substances; that is, the pressure of the vapor in the air is in equilibrium (or is approaching equilibrium) with the vapor pressure of the solid or the solution, as the case may be.

There are many instances of chemical equilibrium analogous to these illustrations of physical equilibrium just cited. A study of the conditions attending or influencing chemical equilibrium has led to an extension of the fundamental principles of chemistry and to the modification of many industrial processes.

It is clear from the foregoing paragraphs that chemical changes are profoundly influenced by those conditions which affect chemical equilibrium. Some of these conditions will now be discussed.

(1) The first is the removal of one of the products of the reaction. Let us reconsider that experiment with iron and steam in which equilibrium is established. If the tube is

opened and a current of steam is introduced, the hydrogen which is formed by the direct action will be forced out and the reaction will continue until the iron is oxidized. That is, the removal of the hydrogen disturbed the equilibrium and thereby permitted the direct action to proceed to completion. Similarly, if hydrogen is introduced into the tube, the steam will be removed and the reduction of the iron by the hydrogen proceeds to completion. In other words, the removal of one product of the reaction upsets the tendency toward equilibrium and allows the reaction to proceed to completion. Constant application is made of this general fact in the laboratory; indeed, in most experiments with gases special care is taken to remove the gaseous product, ostensibly for convenience, but actually to prevent the establishment of chemical equilibrium. For example, in preparing oxygen from mercuric oxide, the latter is heated in an open tube to permit the removal of the oxygen gas, which might under certain conditions recombine by reversal with the liberated mercury. Again, the removal of one product of a reaction is readily accomplished by establishing certain reactions in solutions. If one of the products is an insoluble substance, it is at once removed from the sphere of action. A familiar chemical change illustrates this point. When silver nitrate and hydrochloric acid are dissolved in water, the solution contains at first the ions $Ag^+$, $NO_3^-$, $H^+$, and $Cl^-$, as well as undissociated molecules of silver nitrate ($AgNO_3$) and hydrochloric acid (HCl)—the degree of ionization depending upon the concentration. But the ions $Ag^+$ and $Cl^-$ at once begin to form a precipitate of silver chloride (AgCl), thereby disturbing the equilibrium between the ions and their undissociated molecules. The removal of these ions permits the dissociation of more and more silver nitrate and hydrochloric acid molecules, and the precipitation of silver chloride

continues until the silver or chlorine ions are practically exhausted. If potassium nitrate instead of silver nitrate had been added to hydrochloric acid, no reaction would have taken place, because the equilibrium in the solution would have remained undisturbed. In qualitative analysis tests are purposely chosen to exhibit evidence of a reaction which proceeds (usually) to completion in one direction, and many tests of this kind involve the formation of a precipitate.

(2) The second condition which affects equilibrium is the concentration of one or more of the interacting substances. By concentration is meant the weight of the substance in a given volume; that is, not the absolute quantity, but the relative amount. Moreover, the particular substances whose relative amount is effective are gases and solutes; solids, as a rule, have little or no influence because their concentration is only slightly dependent on changes of temperature and pressure. In the reversible reaction between steam and iron, equilibrium is really dependent on the relative weights of hydrogen and steam, not upon the amounts of solids, iron and iron oxide. If steam or hydrogen is introduced into the tube in which equilibrium exists, the equilibrium is upset because the concentration of one of the effective factors is increased; that is, more steam or more hydrogen in a given volume means greater concentration, and the reaction proceeds accordingly in the proper direction. Similarly, if we wish to prevent or disturb equilibrium, it is only necessary to reduce the concentration of one of the constituents by removing all or part of it. For example, if the hydrogen is removed partly or wholly in the direct reaction between steam and iron, the concentration of the hydrogen is reduced and the direct reaction proceeds undisturbed to completion; removal of steam produces a similar result.

**Equilibrium in Solution.** — The dissociation of acids, bases, and salts in water provides another illustration of equilibrium. Here, however, the equilibrium is between the ions and the undissociated molecules of the solute. When sodium chloride is dissolved in water, equilibrium is immediately established between the ions $Na^+$ and $Cl^-$ and the undissociated molecules NaCl. If water is added or removed, the equilibrium is disturbed, but quickly establishes itself again. That is, reversible reactions occur which can be represented thus: —

$$NaCl \rightleftarrows Na^+ + Cl^-$$

Equilibrium in solution is determined by concentration; *i.e.* by the weight of the dissolved substance in a given volume. Thus, in a solution of sodium chloride containing 5.85 gm. to the liter, equilibrium is maintained by 90 per cent of dissociated molecules and 10 per cent of undissociated molecules. If the volume of the water is changed, the per cent of the dissociated molecules changes, increasing with the addition and decreasing with removal of water. Again, any chemical action which facilitates the removal of ions changes the concentration, disturbs the equilibrium, and often permits a reversible reaction to proceed to completion in one direction. In practice in the laboratory, this change is readily accomplished in several ways. Thus, an insoluble substance may be formed by the combination of two ions and thereby be removed from the sphere of action, or a gaseous substance may be formed by the union of two ions and escape. Again, in saturated or nearly saturated solutions equilibrium may often be disturbed and a reaction started in a direct or reverse direction by the addition of a solution containing any of the kind of ions already in the saturated solution. For example, if silver nitrate or potassium bromate is added to a clear saturated

solution of silver bromate, a precipitate of silver bromate is produced. This precipitation is due to the fact that the addition of silver ions ($Ag^+$) or bromate ions ($BrO_3^-$) increased the concentration of one of the factors, upset the equilibrium, and started the reaction in the direction indicated, thus: —

$$\underset{\text{Silver Ion}}{Ag^+} + \underset{\text{Bromate Ion}}{BrO_3^-} \rightarrow \underset{\text{Silver Bromate}}{AgBrO_3}$$

This reaction continues until equilibrium is restored between silver ions and bromate ions on the one hand and the molecules of silver bromate on the other. Finally, equilibrium in solution may be disturbed by producing in a solution certain ions which unite to form undissociated liquid or gaseous molecules. Thus, in neutralization the essential change, as already stated, is the formation of molecules of water by the union of hydrogen ions ($H^+$) from the acid and hydroxyl ions ($OH^-$) from the base. For instance, when solutions of nitric acid and potassium hydroxide are mixed in the proper proportions, the ions are $H^+$, $NO_3^-$, $K^+$, $OH^-$. Now water is only very slightly dissociated, hence the hydroxyl ions and the hydrogen ions unite to form molecules of water, thereby causing neutralization by removing from the solution the ions characteristic of both acid and base. The ionic equation for the mutual neutralization of nitric acid and potassium hydroxide is —

$$H^+ + NO_3^- + K^+ + OH^- \rightarrow NO_3^- + K^+ + H_2O$$

The simplified ionic equation is —

$$H^+ + OH^- \rightarrow H_2O$$

The subject of reversible reactions and equilibrium is very broad and complicated. Only the simpler aspects have been considered in the foregoing pages. Text-books on physical chemistry must be consulted by those who desire more detailed information.

### Problems and Exercises

1. If a certain current of electricity deposits 2 kg. of copper, how much silver would it deposit?

2. How much heat is liberated in burning 32 gm. of hydrogen in air?

3. Write the ordinary chemical equations for the following reactions: (*a*) Lime (CaO) and water form calcium hydroxide. (*b*) Aluminium and iron oxide ($Fe_2O_3$) form iron and aluminium oxide.

4. When 12 gm. of carbon are burned in oxygen, carbon dioxide is formed and approximately 97,000 cal. are liberated. Write the thermal equation for this reaction.

5. Write the reversible equation expressing the transformation of oxygen into ozone ($O_3$).

## CHAPTER XII

### Chlorine and Hydrochloric Acid

CHLORINE is an important gaseous element, and its compounds are useful, especially hydrochloric acid, sodium chloride, and bleaching powder.

**Occurrence.** — Free chlorine is never found in nature, but its compounds are widely distributed, the most abundant being sodium chloride. Many compounds of chlorine with potassium, magnesium, and calcium are found in the deposits at Stassfurt in Germany. (See Potassium.) About 2 per cent of the total amount of matter in the ocean is chlorine, and the salts found in sea water contain about 55 per cent of chlorine. Silver chloride — " horn " silver — is mined as an ore in the United States and Mexico.

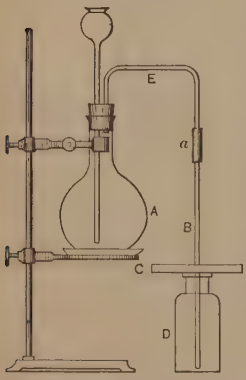



FIG. 23. — Apparatus for preparing chlorine. The gas is generated in *A*, passes through *E* *B* to the bottom of the bottle *D*, and displaces the air, which escapes through a hole in the cover *C*.

**Preparation.** — Chlorine is prepared in the laboratory by heating a mixture of manganese dioxide and hydrochloric acid (Fig. 23). This method was used by Scheele, who discovered the gas in 1774. The equation for the preparation of chlorine is —

$$\underset{\text{Manganese Dioxide}}{MnO_2} + \underset{\text{Hydrochloric Acid}}{4\,HCl} = \underset{\text{Chlorine}}{2\,Cl} + \underset{\text{Manganese Dichloride}}{MnCl_2} + \underset{\text{Water}}{2\,H_2O}$$

This is an oxidizing process, since the hydrogen of the hydrochloric acid is oxidized to water, thereby liberating a part of the chlorine of the acid as free chlorine gas. Other oxidizing substances besides manganese dioxide may be used, such as potassium chlorate ($KClO_3$), potassium dichromate ($K_2Cr_2O_7$), red lead ($Pb_3O_4$), or potassium permanganate ($KMnO_4$).

Sometimes chlorine is prepared in the laboratory by heating a mixture of manganese dioxide, sodium chloride, and sulphuric acid. This method is substantially the same as the other, since a mixture of sulphuric acid and sodium chloride yields hydrochloric acid. The equation for this method of preparing chlorine is —

$$\underset{\text{Sulphuric Acid}}{2\,H_2SO_4} + \underset{\text{Sodium Chloride}}{2\,NaCl} + \underset{\text{Manganese Dioxide}}{MnO_2} = \underset{\text{Chlorine}}{2\,Cl} + \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Manganese Sulphate}}{MnSO_4} + \underset{\text{Water}}{2\,H_2O}$$

Chlorine is manufactured by several processes, one of which (Deacon process) involves the same chemical change (oxidation) as the laboratory method. In the **Deacon process** hydrochloric acid is oxidized by oxygen obtained from the atmosphere. A mixture of hydrochloric acid gas and air is heated to 500° C. and passed through iron tubes containing balls of clay or pieces of brick previously saturated with copper chloride ($CuCl_2$). The essential chemical change is the oxidation of the hydrogen of the hydrochloric acid, and it may be represented by the equation —

$$\underset{\text{Hydrochloric Acid}}{2\,HCl} + \underset{\text{Oxygen}}{O} = \underset{\text{Chlorine}}{2\,Cl} + \underset{\text{Water}}{H_2O}$$

The copper chloride acts as a catalytic agent in this process, and may be replaced by other chlorides.

In the **Weldon process**, an impure native manganese dioxide, known as pyrolusite, is treated with hydrochloric acid in large earthenware retorts or stone tanks heated by hot water or steam. When no more chlorine is liberated, the residue is mainly manganese dichloride.

This "still-liquor" was formerly thrown away, but by the Weldon process it is changed into manganese compounds, which are used to prepare more chlorine. (See Manganese Dioxide.)

Chlorine is also prepared on a large scale by an **electrolytic process.** Sodium chloride is decomposed by electricity in properly constructed electrolytic cells, and the chlorine which is liberated at the anode is conducted off through pipes. Sodium hydroxide is produced at the same time, and the process will be described under this compound.

**Properties.** — Chlorine is a greenish yellow gas. Its color suggested the name *chlorine* (from the Greek word *chloros*, meaning greenish yellow), which was given to it about 1810 by Davy, who spent several years in studying this gas and its compounds. It has a disagreeable, suffocating odor, which is very penetrating. If breathed, it irritates the sensitive lining of the nose and throat, and a large quantity would doubtless cause death. It is heavier than the other elementary gases, and is about 2.5 times heavier than air. Hence it is easily collected by conducting it to the bottom of a bottle and allowing it to displace the air; the term *downward displacement* is sometimes applied to this method of collecting a gas. A liter of dry chlorine at 0° C. and 760 mm. weighs 3.22 gm.

Chlorine is moderately soluble in water, about three liters of the gas dissolving in one liter of water under ordinary conditions. The solution is yellowish, smells strongly of chlorine, and is frequently used in the laboratory as a substitute for the gas. **Chlorine water**, as the solution is called, is unstable even under ordinary conditions, and must be kept in the dark. If the solution is placed in the sunlight, oxygen is soon liberated and hydrochloric acid is formed. Intermediate changes doubtless occur; but the simplest equation for the essential change is —

$$\underset{\text{Water}}{H_2O} + \underset{\text{Chlorine}}{2\,Cl} = \underset{\text{Hydrochloric Acid}}{2\,HCl} + \underset{\text{Oxygen}}{O}$$

Chlorine is much less soluble in a solution of sodium chloride, over which it is sometimes collected. It attacks mercury, and cannot be collected over this liquid.

Chlorine hydrate is formed by cooling concentrated chlorine water, or by passing chlorine into ice water. It is a yellowish, crystalline solid, and in the air it decomposes quickly into chlorine and chlorine water. Its composition corresponds to the formula $Cl_2 . 8 H_2O$.

**Liquid Chlorine** was first prepared by Faraday in 1823. A little chlorine hydrate was inclosed in one arm of a bent tube, which was then sealed. By gently heating the tube, the chlorine hydrate was decomposed into chlorine and water, but the chlorine, being unable to escape, was condensed to a liquid by its own pressure inside the tube. The liquefaction is more easily accomplished, if one end is kept cold during the experiment. This method has been replaced by a simpler one; viz. subjecting the gas to a high pressure and moderately low temperature. The critical temperature is +141° C. and the critical pressure is 84 atmospheres. It is an oily, yellow liquid. Solid chlorine has been obtained as a yellow crystalline mass by cooling the liquid to −102° C.

Chlorine is an active chemical element. It unites directly with most of the elements, the only conspicuous exceptions being oxygen, carbon, and nitrogen. Chlorine does not burn in the air, because it does not form an oxide directly. Many elements unite vigorously with chlorine. Thus, the metals antimony and arsenic, when sprinkled into chlorine, suddenly burst into flame, while the non-metal phosphorus melts at first and finally burns with a feeble flame. If sodium, iron powder, copper wire, or other metals are heated and then put into chlorine, they burn; the sodium and iron produce a dazzling light, and the copper glows and emits dense fumes of whitish smoke. The compound formed in each case is a **chloride**, *i.e.* a compound of chlorine and one other element. (See Chlorides, below.) Chlorine combines readily with hydrogen. Hence, a jet of burning hydrogen when lowered into chlorine continues to burn, forming

hydrochloric acid gas, which appears as a white cloud. The simplest equation for this change is —

$$\underset{\text{Hydrogen}}{H} + \underset{\text{Chlorine}}{Cl} = \underset{\text{Hydrochloric Acid}}{HCl}$$

A mixture of hydrogen and chlorine explodes violently when exposed to the sunlight. Many compounds of hydrogen are decomposed by chlorine. Thus, compounds of hydrogen and carbon, such as those found in illuminating gas, paraffin wax, and wood, burn in chlorine with a smoky flame ; since chlorine does not combine directly with carbon, the flame contains multitudes of very fine particles of solid carbon. A piece of glowing charcoal is extinguished by chlorine. If cotton is saturated with warm turpentine ($C_{10}H_{16}$) and put into a bottle of chlorine, a flame accompanied by a dense cloud of black smoke bursts from the bottle ; the chlorine combines with the hydrogen to form hydrochloric acid, while the carbon is left free.

The power to bleach is the most striking and useful property of chlorine. This property depends upon the fact that chlorine interacts with water and ultimately liberates free oxygen; the latter then decomposes the complex coloring matter into colorless substances. If an envelope on which the postmark, or a pencil mark, is still visible is placed in moist chlorine, these marks will not be bleached because they are largely carbon; but the writing ink, which is substantially a compound of hydrogen, carbon, and iron, will disappear. Litmus paper and many kinds of colored cloth are bleached by moist chlorine. Dry chlorine does not bleach, nor does it combine directly with other substances which are thoroughly dry, or if the chemical change does occur, it is exceedingly slow. Hence it is believed that water serves as a catalytic agent; *i.e.* it hastens a very slow chemical change.

**Uses.** — Chlorine gas is used extensively to manufacture bleaching powder. Liquid chlorine finds application in the manufacture of chlorides and in the extraction of gold from certain ores. Considerable chlorine gas is also used to bleach wood pulp; both gaseous and liquid chlorine are used to remove bromine from its compounds on a large scale.

**Bleaching Powder** is the main source of the chlorine used in the bleaching industries. It is sometimes called "bleach" or "chloride of lime." It is a yellowish white substance having a peculiar odor, which resembles that of chlorine. When dry, it is a powder, but on exposure to the air, it absorbs water and carbon dioxide, becomes lumpy and pasty, and loses some of its chlorine, owing to the formation and liberation of hypochlorous acid (HClO). Acids like sulphuric and hydrochloric acid liberate from bleaching powder its "available chlorine," which varies from 30 to 38 per cent in good qualities. The equations for the interaction of acids and bleaching powder are usually written thus: —

$$\underset{\text{Bleaching Powder}}{CaOCl_2} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = 2\,Cl + \underset{\text{Calcium Sulphate}}{CaSO_4} + H_2O$$

$$CaOCl_2 + \underset{\text{Hydrochloric Acid}}{2\,HCl} = 2\,Cl + \underset{\text{Calcium Chloride}}{CaCl_2} + H_2O$$

The composition of bleaching powder has been much discussed. The most reliable authority gives it the formula $CaOCl_2$. When dissolved in water, bleaching powder forms calcium hypochlorite ($CaO_2Cl_2$) and calcium chloride ($CaCl_2$).

Bleaching powder is manufactured by the interaction of chlorine gas and lime. Lime (calcium oxide, CaO) is carefully slaked with water to form calcium hydroxide ($Ca(OH)_2$). This powder is sifted

into a large absorption chamber made of iron, lead, or tarred brick until the floor is covered with a layer three or four inches deep. The chlorine enters at the top and settles slowly to the floor. The simplest equation for the formation of bleaching powder may be written —

$$\underset{\text{Calcium Hydroxide}}{Ca(OH)_2} + \underset{\text{Chlorine}}{2\,Cl} = \underset{\text{Bleaching Powder}}{CaOCl_2} + \underset{\text{Water}}{H_2O}$$

**Bleaching.** — Immense quantities of bleaching powder are used to whiten cotton and linen goods and paper pulp. The pieces of cotton cloth as they come from the mill are sewed end to end in strips, which are stamped at the extreme ends with some indelible mark to distinguish each owner's cloth. These strips, which are often several miles long, are drawn by machinery into and out of numerous vats of liquors and water, between rollers, and through machines, until they are snow-white and ready to be finished (*i.e.* starched and ironed) or dyed. The whole operation requires three or four days.

The preliminary treatment consists in singeing off the downy pile and loose threads by drawing the cloth over hot copper plates or through a series of gas flames. The object of the remaining operations is threefold: (1) to wash out mechanical impurities, the fatty and resinous matter, and the excess of the different chemicals; (2) to remove matter insoluble in water; and (3) to oxidize the coloring matter by chlorine. The details of the process differ with the texture of the cloth and with its ultimate use. The threefold object above mentioned involves successively "liming," "souring," "chemicking," and "souring," interspersed with frequent washing. The "liming" consists in boiling the cloth in a large kier, or vat, with lime, the "souring" in wetting it with dilute sulphuric or hydrochloric acid, and the "chemicking" in impregnating it with a weak solution of bleaching powder. Often the cloth is boiled at a certain stage with resin and sodium carbonate. The "liming" removes the resinous and the fatty matter, the first "souring" neutralizes traces of lime, and the second, which follows the "chemicking," liberates the chlorine in the fiber of the cloth. Frequent washing is absolutely necessary to remove the impure products of the chemical changes as well as

the excess of lime and other alkali, acid, and chlorine. Should these be left, the cloth would be unevenly bleached, and its fiber would be weak. The cloth is finally treated with an **antichlor**, such as sodium hyposulphite, which removes the last traces of chlorine.

**Chlorides** are formed when chlorine combines with other elements, and they are in general stable compounds. The simplest equations illustrating the combination of chlorine with certain elements are: —

$$\underset{\text{Sodium}}{Na} + \underset{\text{Chlorine}}{Cl} = \underset{\text{Sodium Chloride}}{NaCl}$$

$$\underset{\text{Antimony}}{Sb} + 3\,Cl = \underset{\text{Antimony Trichloride}}{SbCl_3}$$

$$\underset{\text{Copper}}{Cu} + 2\,Cl = \underset{\text{Copper Chloride}}{CuCl_2}$$

$$\underset{\text{Phosphorus}}{P} + 3\,Cl = \underset{\text{Phosphorus Trichloride}}{PCl_3}$$

$$\underset{\text{Hydrogen}}{H} + Cl = \underset{\text{Hydrochloric Acid}}{HCl}$$

Chlorides are an important class of compounds, and they will be considered under the elements with which chlorine combines. (See also Chlorides, below.)

### Hydrochloric Acid

Hydrochloric acid is the common name of a water solution of a very important compound of hydrogen and chlorine, viz. **hydrogen chloride**, HCl. Hydrogen chloride is a gas, which is very soluble in water. This solution is known in commerce as muriatic acid (from the Latin word *muria*, meaning brine), but it is more properly called hydrochloric acid. Hydrogen chloride is often called hydrochloric acid gas.

The early chemists called the gas "spirit of salt." Priestley, who first prepared, collected, and studied the gas, called it "marine acid air." Both expressions emphasize its relation to salt (sodium chloride).

**Occurrence.** — Hydrogen chloride occurs free in volcanic gases. The solution is one constituent of the gastric juice. Chlorides, which are salts of hydrochloric acid, are abundant in the earth's crust and in the ocean.

**Preparation.** — The gas is prepared in the laboratory by the method devised by Glauber in the seventeenth century; viz. by heating concentrated sulphuric acid and sodium chloride. If the mixture is gently heated, the chemical change is represented thus: —

$$\underset{\text{Sodium Chloride}}{NaCl} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Hydrochloric Acid}}{HCl} + \underset{\text{Acid Sodium Sulphate}}{HNaSO_4}$$

But at a high temperature the equation for the reaction is —

$$2\,NaCl + H_2SO_4 = 2\,HCl + \underset{\text{Sodium Sulphate}}{Na_2SO_4}$$

In either case the gas is readily produced. It can be collected over mercury or, more easily, by displacement of air as in the preparation of chlorine. The solution is prepared by passing the gas into water.

**Commercial Hydrochloric Acid** is manufactured in enormous quantities by the method used in the laboratory. A mixture of salt and sulphuric acid is moderately heated in a large hemispherical cast-iron pan, and the gas conducted through an earthenware pipe into an absorbing tower; the fused mass of acid sodium sulphate and salt is then subjected to a higher temperature, and the remainder of the gas is led into the absorbing tower. These towers are

high and filled with coke or pieces of brick over which water trickles; as the hydrochloric acid gas passes up the tower, it is absorbed by the descending water, and concentrated acid flows from the bottom of the tower. The gas is usually cooled before it enters the towers. Sometimes the gas is conducted through huge earthenware jars before entering the towers. In these jars the gas and water are caused to flow constantly in opposite directions, thus insuring complete absorption. Hydrochloric acid can be manufactured synthetically, *i.e.* by burning hydrogen gas in chlorine gas. The equation for this reaction is —

$$\underset{\text{Hydrogen}}{H} + \underset{\text{Chlorine}}{Cl} = \underset{\text{Hydrochloric Acid}}{HCl}$$

**Properties.** — Hydrochloric acid gas is colorless. When it escapes into moist air, it forms fumes which are really minute drops of a solution of the gas in the moisture of the air. It has a choking, sharp taste, and irritates the lining of the nose and throat. The gas does not burn nor support combustion. It is about 1.25 times heavier than air, and may therefore be collected by displacement of air, like chlorine. One liter at 0° C. and 760 mm. weighs 1.641 gm. The critical temperature is + 52° C., and the gas becomes a colorless liquid when subjected to a high pressure and moderately low temperature. The extreme solubility of hydrochloric acid gas in water is one of its most striking properties. One liter of water will dissolve about 550 l. of gas, if both are at 0° C. and 760 mm. At the ordinary temperature about 500 l. of gas dissolve in 1 l. of water, and as the temperature rises, the solubility decreases. The solution is the familiar **hydrochloric acid.** The gas readily escapes, hence the acid forms fumes when exposed to the air. Pure hydrochloric acid is a colorless liquid, but the commercial acid has a yellow color, usually due to iron

compounds or to dissolved chlorine. Like the common acids, its solution reddens blue litmus and yields hydrogen by interaction with certain metals. In terms of the theory of electrolytic dissociation, hydrochloric acid is a strong acid; *i.e.* it dissociates to a considerable extent into ions, one kind being $H^+$, the other being $Cl^-$.

The most concentrated acid contains about 40 per cent (by weight) of the compound (HCl), and its specific gravity is 1.2. When the concentrated acid is heated, the gas is evolved until the solution contains about 20 per cent of the acid, and then the liquid boils at 110° C. without further change. The dilute acid, on the other hand, loses water until the same conditions prevail.

**Uses of Hydrochloric Acid.** — Vast quantities are used to prepare the chlorine consumed in the manufacture of bleaching powder. Various chlorides are prepared from it, and it is one of the common acids used in the chemical laboratory and in many industries.

**Chlorides** are formed by direct addition of chlorine to metals, as we have seen. They are also formed by the substitution of a metal for the hydrogen in hydrochloric acid. Chlorides, therefore, are salts of hydrochloric acid. They can be prepared in several ways, *e.g.* (1) by the interaction of hydrochloric acid and metals, metallic oxides, or hydroxides, and (2) by the interaction of certain salts and hydrochloric acid or chlorides. The following equations illustrate several of these methods: —

$$\underset{\text{Zinc}}{Zn} + 2\,HCl = \underset{\substack{\text{Zinc}\\\text{Chloride}}}{ZnCl_2} + 2\,H$$

$$\underset{\substack{\text{Zinc}\\\text{Oxide}}}{ZnO} + 2\,HCl = \underset{\substack{\text{Zinc}\\\text{Chloride}}}{ZnCl_2} + H_2O$$

$$\underset{\text{Zinc Hydroxide}}{Zn(OH)_2} + 2\,HCl = \underset{\text{Zinc Chloride}}{ZnCl_2} + 2\,H_2O$$

$$\underset{\text{Silver Nitrate}}{AgNO_3} + HCl = \underset{\text{Silver Chloride}}{AgCl} + \underset{\text{Nitric Acid}}{HNO_3}$$

One molecule of a chloride may contain several atoms of chlorine. Often the name of the compound indicates this fact; *e.g.* manganese dichloride ($MnCl_2$), antimony trichloride ($SbCl_3$), phosphorus trichloride and pentachloride ($PCl_3$ and $PCl_5$). If a metal forms two chlorides, the two are distinguished by modifying the name of the metal; the one containing the smaller proportions of chlorine ends in *-ous*, the one containing the larger ends in *-ic*. Thus, mercurous chloride is HgCl, but $HgCl_2$ is mercuric chloride. Similarly, we have ferrous chloride, $FeCl_2$, and ferric chloride, $FeCl_3$.

**The Test for Hydrochloric Acid and Chlorides.** — Most chlorides are soluble in water, those of lead, silver, and mercury (-ous) being the only conspicuous exceptions. If silver nitrate is added to hydrochloric acid or to the solution of a chloride, a white, curdy precipitate of silver chloride is formed, which (*a*) is insoluble in nitric acid, (*b*) soluble in warm ammonium hydroxide, and (*c*) turns purple in the sunlight. The invariable formation of silver chloride is the test for hydrochloric acid and soluble chlorides. This chemical change is a typical illustration of double decomposition. The equation for the chemical change is —

$$\underset{\text{Hydrochloric Acid}}{HCl} + \underset{\text{Silver Nitrate}}{AgNO_3} = \underset{\text{Silver Chloride}}{AgCl} + \underset{\text{Nitric Acid}}{HNO_3}$$

By an inspection of this equation we see that both the hydrochloric acid and silver nitrate decompose and the chemical fragments, so to speak, recombine in a different way to

form the two products. The same test is applicable to hydrochloric acid and a chloride, because both yield chlorine ions ($Cl^-$). The test is for ionic chlorine, and the general ionic equation may be written thus : —

$$Cl^- + Ag^+ \rightarrow AgCl$$

**Miscellaneous.** — Besides hydrochloric acid, there are four other acids of chlorine ; they contain oxygen as well as hydrogen. These acids are hypochlorous acid ($HClO$), chlorous acid ($HClO_2$), chloric acid ($HClO_3$), and perchloric acid ($HClO_4$). They are prepared with difficulty, and decompose readily. Thus, hypochlorous acid is prepared by the interaction of dilute hydrochloric acid and sodium hypochlorite ($NaClO$), but the procedure must be careful, because the resulting hypochlorous acid itself is decomposed by hydrochloric acid. Hypochlorous acid also decomposes when its solution is warmed or exposed to the sunlight, oxygen gas and hydrochloric acid being the products. This acid ($HClO$) is formed to a slight extent when chlorine dissolves in water, thus : —

$$\underset{\text{Chlorine}}{2\,Cl} + \underset{\text{Water}}{H_2O} = \underset{\text{Hypochlorous Acid}}{HClO} + \underset{\text{Hydrochloric Acid}}{HCl}$$

But the hypochlorous acid decomposes readily and under many conditions, especially when exposed to the sunlight; the equation for the reaction in the last-named case may be written : —

$$\underset{\text{Hypochlorous Acid}}{HClO} = \underset{\text{Oxygen}}{O} + \underset{\text{Hydrochloric Acid}}{HCl}$$

It is this free oxygen which is the effective agent in bleaching, though the unstable hypochlorous acid is the way station, so to speak, between the chlorine and the oxygen.

The corresponding salts of two of the oxy-chlorine acids

are important, viz. the hypochlorites and chlorates. Solutions of potassium hypochlorite (Javelle's water) and sodium hypochlorite (Labarraque's solution) find application in the removal of stains from cotton and linen goods; "bleach liquors" consisting largely of hypochlorites are used as bleaching agents in some industries. Chlorates of potassium and sodium are used as a source of oxygen.

Chlorine forms two oxides — chlorine monoxide ($Cl_2O$) and chlorine dioxide ($ClO_2$). Each is an unstable yellowish brown gas.

### Problems and Exercises

**1.** One equation for the preparation of chlorine is —

$$\begin{array}{rcrcrcrcr} 4\,HCl & + & MnO_2 & = & 2\,Cl & + & MnCl_2 & + & 2\,H_2O \\ 146 & + & 87 & = & 71 & + & 126 & + & 36 \end{array}$$

(*a*) How many grams of chlorine can be made from 247 gm. of manganese dioxide? (*b*) Name all the products.

2. How much sodium chloride is needed to prepare a kilogram of hydrochloric acid gas?

3. How many grams of manganese dioxide are necessary to prepare 100 gm. of chlorine from hydrochloric acid?

4. Calculate the percentage composition of (*a*) hydrochloric acid gas, (*b*) sodium chloride, (*c*) silver chloride (AgCl), (*d*) potassium chloride (KCl).

5. Write equations for the following reactions by applying the method outlined in Chapter VII: (*a*) Phosphorus and chlorine form phosphorus trichloride. (*b*) Phosphorus trichloride and chlorine form phosphorus pentachloride. (*c*) Aluminium and hydrochloric acid form hydrogen and aluminium chloride.

6. Write the ionic equation for the interaction of hydrochloric acid and silver nitrate.

Jan. 21, 1916.

## CHAPTER XIII

### Compounds of Nitrogen — Gay-Lussac's Law

THE most important compounds of nitrogen are ammonia ($NH_3$), nitric acid ($HNO_3$), and compounds related to them. Many animal and vegetable substances essential to life are compounds of nitrogen.

### AMMONIA

**The term ammonia** includes both the gas and its solution in water, though the latter is more accurately called **ammonium hydroxide.**

**Formation of Ammonia.** — When vegetable and animal matter containing nitrogen decomposes or decays, the nitrogen and hydrogen are liberated in combination, as ammonia. The odor of ammonia is often noticed near stables. If animal matter containing nitrogen is heated, ammonia is given off. The old custom of preparing ammonia by heating horns and hoofs in a closed vessel, *i.e.* by dry distillation, gave rise to the term "spirits of hartshorn." Soft coal contains compounds of nitrogen and of hydrogen, and when the coal is heated to make illuminating gas, one of the products is ammonia.

**Preparation.** — Ammonia gas is prepared in the laboratory by heating ammonium chloride with a base, the mild base calcium hydroxide being usually used. The equation for the reaction is —

| $2\,NH_4Cl$ | + | $Ca(OH)_2$ | = | $2\,NH_4OH$ | + | $CaCl_2$ |
|---|---|---|---|---|---|---|
| Ammonium Chloride | | Calcium Hydroxide | | Ammonium Hydroxide | | Calcium Chloride |

But the ammonium hydroxide is unstable and decomposes into ammonia gas and water, thus:—

$$\underset{\text{Ammonium Hydroxide}}{NH_4OH} = \underset{\text{Ammonia Gas}}{NH_3} + \underset{\text{Water}}{H_2O}$$

The ammonia gas is very volatile and is usually collected by allowing it to flow into an inverted bottle and displace the air (Fig. 24); the term *upward displacement* is sometimes applied to this method of collecting a gas. The solution is prepared by conducting the gas into water.

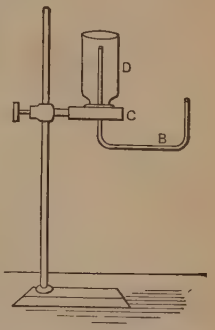



FIG. 24. — Apparatus for collecting ammonia gas. The gas from the generator flows through the delivery tube *B* to the top of the bottle *D* and displaces the air, which escapes through the hole in the block *C*.

The main source of the **ammonia of commerce** is the ammoniacal liquor or gas liquor of the illuminating gas works. The gases which come from the retorts in which the coal is heated are passed into water, which absorbs the ammonia and certain other gases. This impure gas liquor is treated with an alkali to liberate the ammonia, which is absorbed in tanks containing hydrochloric acid or sulphuric acid. This solution upon the addition of an alkali (such as calcium hydroxide) gives up its ammonia, which is dissolved in distilled water, forming thereby the **ammonium hydroxide** or **aqua ammoniæ** of commerce.

**Properties of Ammonia.** — Ammonia gas is colorless. It has an exceedingly pungent odor, and if inhaled suddenly or in large quantities it brings tears to the eyes and may cause suffocation. It is a light, volatile gas, being only .59 times as heavy as air. A liter of the gas at 0° C. and 760 mm. weighs about .77 gm. It will not burn in the air under ordinary conditions, nor will it support the combustion

of a blazing stick; but if the air is heated, or if its proportion of oxygen is increased, a jet of ammonia gas will burn in it with a yellowish flame, thereby illustrating the broader application of the term *combustion*.

Ammonia gas is easily liquefied, since its critical temperature is about +130° C.; at 0° C. a pressure of about 4.2 atmospheres causes liquefaction. At about −76° C. a white solid is produced. **Liquefied ammonia** is often called **anhydrous ammonia**, because it contains no water. It boils at about −33.5° C. Hence, if it is exposed to the air or warmed in any way, it changes back to a gas, and in doing so absorbs considerable heat. This fact has led to the extensive use of liquid ammonia in the manufacture of ice.

When electric sparks are passed through ammonia gas, it decomposes into nitrogen and hydrogen. But if a mixture of nitrogen and hydrogen is sparked, these gases combine to form ammonia gas. In neither case, however, is the reaction complete. The final mixture always contains about 98 per cent of nitrogen and hydrogen, and 2 per cent of ammonia gas. That is, the reaction is reversible and proceeds until equilibrium is reached. The simplest equation for this reversible reaction is —

$$NH_3 \rightleftarrows N + 3\,H$$

If water or acid is added during the sparking of the mixture of nitrogen and hydrogen, the ammonia is dissolved. Its removal upsets the equilibrium, and the reaction then proceeds to completion; *i.e.* all the nitrogen and hydrogen combine.

Another marked property of ammonia gas is its solubility in water. A liter of water at 0° C. dissolves 1148 l. of gas (measured at 0° C. and 760 mm.), and at the ordinary temperature 1 l. of water dissolves about 700 l. of gas. This

solution of the gas is usually called **ammonia**, though other names are often applied to it; *i.e.* **ammonium hydroxide, aqua ammoniæ**, or **ammonia water.** It gives off the gas freely, especially when heated, as may easily be discovered by the odor or by the formation of the dense white fumes of solid ammonium chloride ($NH_4Cl$) when the solution is exposed to hydrochloric acid. The volatility of ammonia was early detected, and the name volatile alkali was applied to it; the discoverer, Priestley, called the gas alkaline air. The gas can be completely removed from solution by boiling. The commercial solution is lighter than water (its specific gravity being about .88) and contains about 35 per cent (by weight) of the gas. Ammonium hydroxide has an alkaline reaction, neutralizes acids and forms salts, and acts in many respects like sodium hydroxide. In terms of the theory of electrolytic dissociation, ammonium hydroxide is a weak base; *i.e.* it dissociates only to a slight degree into ions ($NH_4^+$ and $OH^-$).

**Ammonium Compounds.** — When ammonia gas is passed into water, some of the gas combines with the water and forms a solution of an unstable compound called **ammonium hydroxide.** Its formation may be represented thus: —

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Ammonium}\\\text{Hydroxide}}}{NH_4OH}$$

Ammonia ($NH_3$) also unites directly with acids, thereby forming salts, thus: —

$$\underset{\text{Gas}}{\underset{\text{Ammonia}}{NH_3}} + \underset{\text{Acid}}{\underset{\text{Hydrochloric}}{HCl}} = \underset{\text{Chloride}}{\underset{\text{Ammonium}}{NH_4Cl}}$$

Analogous salts are ammonium sulphate and ammonium nitrate.

Ammonium hydroxide is a base. It neutralizes acids and forms salts, thus: —

$$NH_4OH + HCl = \underset{\text{Ammonium Chloride}}{NH_4Cl} + H_2O$$

$$2\,NH_4OH + H_2SO_4 = \underset{\text{Ammonium Sulphate}}{(NH_4)_2SO_4} + 2\,H_2O$$

These salts, ammonium chloride and ammonium sulphate, are strictly analogous to sodium salts. Thus, we have —

| Sodium Salts | Ammonium Salts |
|---|---|
| $NaCl$ | $NH_4Cl$ |
| $NaNO_3$ | $NH_4NO_3$ |
| $Na_2SO_4$ | $(NH_4)_2SO_4$ |
| etc. | etc. |

Hence, it is believed that ammonium compounds contain a group of atoms which acts chemically like an atom of a metal. This group of atoms is called **ammonium**, and its formula is $NH_4$. Ammonium has never been separated from its compounds, or if it has, it is so unstable that it immediately decomposes into ammonia gas and hydrogen. So also ammonium hydroxide has never been obtained free, for it decomposes readily into ammonia gas and water, thus: —

$$\underset{\text{Ammonium Hydroxide}}{NH_4OH} = \underset{\text{Ammonia Gas}}{NH_3} + \underset{\text{Water}}{H_2O}$$

But the properties of ammonium hydroxide leave no doubt but that it is a compound of hydroxyl and a metallic group of atoms, just as sodium hydroxide is a compound of hydroxyl and the metal sodium. Ammonium is sometimes called a **radical**, because it is the root or foundation of a series of compounds. It is likewise called a hypothetical metal, because its existence is assumed, and it acts chemically like a metal.

**Uses of Ammonium Hydroxide.** — Ammonium hydroxide is widely used as a cleansing agent (especially for the removal of grease), as a restorative in cases of fainting or of inhaling irritating gases, in dyeing, and calico printing, and in the manufacture of dyestuffs, sodium bicarbonate, and ammonium compounds. Its salts have many domestic, industrial, and agricultural uses. (See Chapter XXV.)

**The Use of Ammonia as a Refrigerant and in making Ice** depends upon the fact that many liquids in changing into a gas absorb heat. Liquefied ammonia (not the ordinary ammonia water) changes rapidly into a gas when its temperature is raised or the pressure reduced. Hence, if liquefied ammonia is allowed to flow through a pipe immersed in a solution of sodium chloride or calcium chloride (technically called a brine), the ammonia evaporates in the pipe and cools the brine, which may be used directly as a refrigerant or for making ice. In some cold-storage plants, breweries, packing houses, and sugar refineries, this cold brine is pumped through pipes placed in the rooms where a low temperature is desired.

The construction and operation of an ice-making plant are essentially as follows: —

Liquefied ammonia is forced from a tank into a series of pipes which are submerged in an immense vat filled with brine. Large galvanized iron cans containing pure water to be frozen are immersed in the brine, which is kept below the freezing point of water by rapid evaporation of the ammonia in the pipes. After several hours the water in the cans is frozen into ice. As fast as the ammonia gas forms in the pipes, it is removed by exhaust pumps into another tank, where it is recondensed to liquefied ammonia and conducted, as needed, into the first tank ready for renewed use. The ammonia is thus used over and over without appreciable loss. The pure water is sometimes obtained by condensing the exhaust steam from the boilers used to operate the machinery, though it usually comes from a deep well. Most ocean steamers have an ice plant, and in large cities in warm climates manufactured ice is a common commodity.

**Composition of Ammonia Gas.** — Many facts show that ammonia gas is composed of nitrogen and hydrogen in the ratio of 1 to 3 by volume and 14 to 3 by weight. The **volumetric composition** is shown in two ways. The first depends upon the fact that ammonia and chlorine interact thus: —

Fig. 25. — Apparatus for determining the composition of ammonia gas.

$$\underset{\text{Ammonia Gas}}{2\,NH_3} + \underset{\text{Chlorine}}{3\,Cl_2} = \underset{\text{Nitrogen}}{N_2} + \underset{\text{Hydrochloric Acid}}{6\,HCl}$$

A tube (Fig. 25) filled with a known volume of chlorine is provided with a funnel through which concentrated ammonium hydroxide is dropped into the chlorine, until the reaction ceases. After the excess of ammonia is neutralized with sulphuric acid, the volume of nitrogen left is found to be one third of the original volume of chlorine gas. Now hydrogen and chlorine combine in equal volumes; hence, the volume of hydrogen withdrawn from the added ammonia must be equal to the original volume of chlorine. But this volume is three times the volume of nitrogen; therefore there is three times as much hydrogen as nitrogen by volume in ammonia gas.

The **gravimetric composition** of ammonia gas is found by oxidizing it, and weighing the water and nitrogen, which are the only products. The results show that fourteen parts of nitrogen combine with three parts of hydrogen.

## Nitric Acid

**Nitric Acid** is one of the most useful compounds of nitrogen. It was known to the alchemists, who used it to prepare a mixture which dissolves gold. (See Aqua Regia, below.) Nitric acid is used in the preparation of many nitrogen compounds.

**Formation of Nitric Acid.** — When moist animal or vegetable matter containing nitrogen decays in the presence of an alkali, nitric acid is formed; but it is neutralized at once by the alkali, so nitrates — salts of nitric acid — are the final products. This chemical change is known as **nitri-**

fication, and it is caused, or largely influenced, by minute living organisms called bacteria. Nitrification is constantly going on in the soil and is an exceedingly helpful process, since it transforms harmful waste matter into valuable plant food. As a result of nitrification, there are vast deposits of nitrates, especially in the desert regions and tropical countries. For example, potassium nitrate ($KNO_3$) is found in the soils near large cities in India, Persia, and Egypt.

Nitric acid is formed in small quantities when electric sparks are passed through moist air. Hence nitric acid or its salts can be detected in the atmosphere after a thunder storm. This chemical change is now being applied on a large scale. Electric sparks are passed through confined air and the products are forced into a tower. Here they are absorbed in water or in a mixture of water and lime, thereby forming nitric acid or a calcium salt of this acid.

**Preparation.** — Nitric acid is prepared in the laboratory by heating concentrated sulphuric acid with a nitrate, usually sodium or potassium nitrate. About equal weights of the nitrate and acid are put into a glass retort and gently heated; the nitric acid distills into a receiver, which is kept cool by water, ice, or moist paper. The chemical change at a low temperature is represented by the equation —

$$\underset{\text{Sodium Nitrate}}{NaNO_3} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Nitric Acid}}{HNO_3} + \underset{\text{Acid Sodium Sulphate}}{HNaSO_4}$$

But if the temperature is high and an excess of the nitrate is present, the equation is: —

$$2\,NaNO_3 + H_2SO_4 = 2\,HNO_3 + Na_2SO_4$$

At a high temperature, however, part of the nitric acid decomposes, hence excessive heat is usually avoided.

Nitric acid is manufactured on a large scale by heating sodium nitrate and sulphuric acid in a large cast-iron retort connected with huge glass or earthenware bottles; the last bottle is connected with a tower filled with coke over which water trickles to absorb the vapors which escape from the bottles. The acid vapors are also often condensed in earthenware or glass tubes.

**Properties.** — Pure nitric acid is a colorless liquid, but the commercial acid is yellow or reddish, owing to absorbed nitrogen compounds, chlorine, or iron compounds. It decomposes slowly in the sunlight or when heated, and a brownish gas may often be seen in bottles of nitric acid. It absorbs water, and forms irritating fumes when exposed to the air. The specific gravity of the commercial acid is about 1.42, and it contains from 60 to 70 per cent of the real acid ($HNO_3$), the rest being water. If the water is removed by slowly distilling the commercial acid with concentrated sulphuric acid, the product contains from 94 to 99 per cent of the real acid, and its specific gravity is about 1.51. When nitric acid is boiled, it loses either acid or water until the liquid contains approximately 68 per cent of nitric acid, and then it continues to boil unchanged at 120° C. (See Hydrochloric Acid.)

A solution of nitric acid has the properties of acids to a marked degree. In terms of the theory of electrolytic dissociation it is one of the strongest acids; *i.e.* it dissociates readily into ions, one kind being $H^+$, the other being $NO_3^-$.

Nitric acid is very corrosive. It turns the skin a yellow color, and may cause serious burns. Many organic substances are turned yellow and sometimes completely decomposed by it. It parts readily with its oxygen, especially when hot, and is therefore an energetic oxidizing agent. Glowing charcoal continues to burn in the acid, while straw,

sawdust, hair, and similar substances are charred and even inflamed by it. Iron sulphide (FeS) heated with nitric acid becomes oxidized to iron sulphate ($FeSO_4$). It interacts readily and often violently with metals, metallic oxides, and hydroxides, forming a variety of products, especially nitrates.

**Uses of Nitric Acid.** — Nitric acid is one of the common laboratory acids. Large quantities are used in the manufacture of nitrates, dyestuffs, sulphuric acid, nitroglycerine, and guncotton, and in the refining of gold and silver.

**Nitrates.** — Nitric acid is monobasic and forms a series of well-defined salts called **nitrates.** The interaction of nitric acid and most metals is exceedingly vigorous, and for this reason, probably, the alchemists called the acid *aqua fortis* — strong water. The reaction varies with the metal, concentration of the acid, temperature, and the presence of resulting compounds; it is often quite complex.

The solid product of the reaction is usually a soluble nitrate, though some metals, such as tin and antimony, form insoluble oxides. The gaseous products are usually oxides of nitrogen, especially nitric oxide (NO), which, however, quickly forms nitrogen peroxide ($NO_2$) in the air. Hydrogen is never liberated so that it can be collected; it immediately reduces the nitric acid to other compounds of nitrogen. Ammonia gas ($NH_3$), and even nitrogen, are formed under certain circumstances. The interaction between nitric acid and copper will serve as an illustration of one of the common reactions. When dilute nitric acid is poured upon copper, the liquid bubbles violently and becomes hot, a dense reddish brown gas is given off, and the liquid turns blue, owing to the dissolved copper nitrate. Other metals, such as zinc, iron, and silver, act in a similar way, though

the nitrate is blue only in the case of copper. The equation for the reaction between dilute nitric acid and copper is —

$$3\,Cu + 8\,HNO_3 = \underset{\text{Copper Nitrate}}{3\,Cu(NO_3)_2} + \underset{\text{Nitric Oxide}}{2\,NO} + 4\,H_2O$$

Nitric oxide is colorless, but when exposed to the air, it changes at once into the reddish brown peroxide, thus: —

$$\underset{\text{Nitric Oxide}}{2\,NO} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Nitrogen Peroxide}}{2\,NO_2}$$

Nitrates, as a rule, are very soluble in water. They behave in various ways when heated. Some, like sodium and potassium nitrates, lose oxygen and pass into **nitrites**; others, like copper nitrate, form an oxide of the metal, an oxide of nitrogen, and oxygen; and one, ammonium nitrate, decomposes into water and nitrous oxide ($N_2O$). Since many nitrates, when heated, give up oxygen, they are powerful oxidizing agents. Potassium nitrate dropped on hot charcoal burns the charcoal vigorously and rapidly. This kind of chemical action is called **deflagration.** Nitrates have numerous uses, and these, as well as their special properties, will be treated under their respective metals.

**The Test for Nitrates** (and of course for **nitric acid**) is as follows: Add to the nitric acid or the solution of the nitrate an equal volume of concentrated sulphuric acid, and cool the mixture. Upon the cool mixture pour carefully a cold, dilute solution of freshly prepared ferrous sulphate. A dark brown layer appears where the two liquids meet, owing to the formation of a brown unstable compound whose composition is not well understood, but is approximately $3\,FeSO_4 . 2\,NO$.

**Nitrous Acid**, $HNO_2$, is not easily obtained in the free state owing to its instability, but its salts — the **nitrites** — are well known. Potassium nitrite ($KNO_2$) and sodium nitrite ($NaNO_2$) are formed by removing the oxygen from the corresponding nitrate by heating alone or with lead. Nitrites give off brown fumes ($NO_2$) when treated with sulphuric acid, and are thus readily distinguished from nitrates. Nitrites are used in the manufacture of certain dyestuffs.

## Oxides of Nitrogen

There are five oxides of nitrogen: —

| Name | Formula |
|---|---|
| Nitrous Oxide | $N_2O$ |
| Nitric Oxide | $NO$ |
| Nitrogen Trioxide | $N_2O_3$ |
| Nitrogen Peroxide | $NO_2$ |
| Nitrogen Pentoxide | $N_2O_5$ |

Only three of these are important; viz. nitrous oxide, nitric oxide, and nitrogen peroxide.

**Nitrous Oxide**, $N_2O$, is one of the numerous decomposition products of nitric acid, but it is usually prepared by decomposing ammonium nitrate. This salt, if gently heated, first melts and then decomposes into nitrous oxide and water; the gas can be collected over water, preferably warm water. The equation for the chemical change is —

$$\underset{\text{Ammonium Nitrate}}{NH_4NO_3} = \underset{\text{Nitrous Oxide}}{N_2O} + \underset{\text{Water}}{2\,H_2O}$$

This colorless gas has a sweet taste and a faint but pleasant odor. It is less soluble in hot than in cold water. The

gas does not burn, but it supports the combustion of many burning substances, though not so vigorously as oxygen does. Sulphur, for example, will not burn in nitrous oxide, unless the sulphur is hot and well ignited at first; very fine iron wire, if well ignited, burns in the gas, but the combustion is not so conspicuous as in oxygen. The products of the chemical change are oxides and nitrogen. The most striking property of nitrous oxide is its effect on the human system. If breathed for a short time, it causes more or less nervous excitement, sometimes manifested by laughter. The gas was called "laughing gas" by Davy. If breathed in large quantities, it slowly produces unconsciousness. The gas is often administered when unconsciousness is desired for a short time, as in dentistry. It is easily liquefied by cold, by pressure, or by both together, since its critical temperature is about $+37°$ C. It is often used in liquid form to furnish the gas itself and to produce low temperatures.

Nitrous oxide was discovered by Priestley in 1776; but its composition was not explained until 1799, when Davy, by an extensive study of its properties, proved it to be an oxide of nitrogen. In his enthusiasm Davy wrote a friend: "This gas raised my pulse upward of twenty strokes, made me dance about the laboratory as a madman, and has kept my spirits in a glow ever since." It is needless to say that the usual results are more quieting.

**Nitric Oxide**, NO, has long been known, since it is the usual gaseous product formed by the interaction of nitric acid and metals. It is conveniently prepared by the interaction of copper and dilute nitric acid (sp. gr. 1.2). The equation for the complex chemical change is written thus: —

$$\underset{\text{Copper}}{3\,Cu} + \underset{\substack{\text{Nitric}\\\text{Acid}}}{8\,HNO_3} = \underset{\substack{\text{Nitric}\\\text{Oxide}}}{2\,NO} + \underset{\substack{\text{Copper}\\\text{Nitrate}}}{3\,Cu(NO_3)_2} + 4\,H_2O$$

The gas thus prepared is impure, and it is customary to use ferrous sulphate and nitric acid as a source of the pure gas.

Nitric oxide is a colorless gas, but upon exposure to the air it combines at once with oxygen, forming dense reddish brown fumes of nitrogen peroxide. The equation for this change is —

$$\underset{\text{Nitric Oxide}}{2\,NO} + O_2 = \underset{\text{Nitrogen Peroxide}}{2\,NO_2}$$

This property distinguishes nitric oxide from all other gases. It does not burn, nor does it support combustion unless the burning substance (*e.g.* phosphorus or sodium) introduced is hot enough to decompose the gas into nitrogen and oxygen, and then, of course, the liberated oxygen supports the combustion. It is only slightly soluble in water.

**Nitrogen Peroxide**, $NO_2$, is the reddish gas formed by the direct combination of nitric oxide and oxygen. Thus: —

$$\underset{\text{Nitric Oxide}}{2\,NO} + O_2 = \underset{\text{Nitrogen Peroxide}}{2\,NO_2}$$

It is also produced by heating certain nitrates. Thus: —

$$\underset{\text{Lead Nitrate}}{Pb(NO_3)_2} = \underset{\text{Nitrogen Peroxide}}{2\,NO_2} + \underset{\text{Lead Oxide}}{PbO} + \underset{\text{Oxygen}}{O}$$

The fumes of nitrogen peroxide usually appear when nitric acid and metals interact, but, as already stated, the fumes are not produced at first, being the result of a second chemical change when the real product, nitric oxide, comes in contact with oxygen of the air.

Nitrogen peroxide has a disagreeable odor, and if breathed in moderately large quantities, it is poisonous. It dissolves in water, and yields with cold water a mixture of nitrous and nitric acids. It also dissolves in concentrated nitric acid, forming **fuming nitric acid**, which is a powerful oxidizing agent.

At about −12° C. nitrogen peroxide is a colorless solid. At about −10° C. it is a yellowish liquid, and as the temperature rises, the color grows darker, until at 22° C. the liquid boils and gives off the familiar reddish brown gas. Above 140° C. this brown gas begins to lose its color; at higher temperatures the brown color almost entirely disappears, and nitric oxide (NO) and oxygen are produced. Experiments show that the reddish brown gas at about 140° C. has the formula $NO_2$, while the formula of the nearly colorless gas at about 22° C. is $N_2O_4$. The relation of these two gases is strikingly shown by collecting some nitrogen peroxide in a glass tube, closing the tube, and immersing the lower half in ice water. The lower part becomes pale brown, whereas the upper is reddish brown (particularly if the tube is heated before immersion).

**Nitrogen Trioxide**, $N_2O_3$, and **Nitrogen Pentoxide**, $N_2O_5$, are unstable compounds and have no practical importance. They are the anhydrides of nitrous and nitric acids, thus: —

$$\underset{\text{Nitrogen Trioxide}}{N_2O_3} + H_2O = \underset{\text{Nitrous Acid}}{2\,HNO_2}$$

$$\underset{\text{Nitrogen Pentoxide}}{N_2O_5} + H_2O = \underset{\text{Nitric Acid}}{2\,HNO_3}$$

**Aqua Regia** is an old term which is still applied to a mixture of concentrated nitric and hydrochloric acids. The expression means "royal water," and indicates that the mixture dissolves gold (a "noble" metal), which is insoluble in either acid alone. Its solvent power depends mainly upon the free chlorine which is produced in the mixture by the oxidizing action of the nitric acid. The product of the action of **aqua regia** on metals is always a chloride of the metal.

## Gay-Lussac's Law of Gas Volumes

Several gaseous compounds of nitrogen illustrate Gay-Lussac's law of gas volumes. Experiment shows the following facts about these gases and certain others previously studied: —

COMBINATION OF GASES BY VOLUME

| VOLUMES OF COMBINING GASES | VOLUMES OF GASEOUS PRODUCTS |
|---|---|
| 2 vol. hydrogen<br>1 vol. oxygen | 2 vol. water vapor |
| 1 vol. hydrogen<br>1 vol. chlorine | 2 vol. hydrochloric acid gas |
| 3 vol. hydrogen<br>1 vol. nitrogen | 2 vol. ammonia gas |
| 2 vol. nitrogen<br>1 vol. oxygen | 2 vol. nitrous oxide gas |
| 1 vol. nitrogen<br>1 vol. oxygen | 2 vol. nitric oxide gas |
| 1 vol. nitrogen<br>2 vol. oxygen | 2 vol. nitrogen peroxide gas |
| 2 vol. nitrogen<br>3 vol. oxygen | 2 vol. nitrogen trioxide gas |

It is clear from the above table that small whole numbers express the relation existing between the volumes of the combining gases and the volume of the gaseous product. This simple relation is general and was summarized in 1808 by the French chemist Gay-Lussac in the form of a law, thus: —

*Gases combine in volumes which bear a simple numerical ratio to each other and to the volume of their gaseous product.*

Additional illustrations of this fundamental law will be given in subsequent chapters. (See especially Chapters XV and XVI (oxides of carbon and hydrocarbons.) See also gas equations, Chapter XIV.)

PROBLEMS

1. How many grams of ammonia gas can be obtained from 2140 gm. of ammonium chloride by heating with lime?

2. Calculate the percentage composition of (*a*) ammonium chlo-

ride, (*b*) ammonium hydroxide, (*c*) ammonium sulphate, (*d*) ammonium nitrate.

3. Calculate the simplest formula of the compounds having the percentage composition (*a*) N = 82.35, H = 17.64; and (*b*) N = 26.17, Cl = 66.35, H = 7.48.

4. Calculate the percentage composition of (*a*) nitric acid, (*b*) potassium nitrate ($KNO_3$), (*c*) sodium nitrate.

5. How many grams of nitric acid can be obtained by heating a kilogram of sodium nitrate with sulphuric acid at a low temperature?

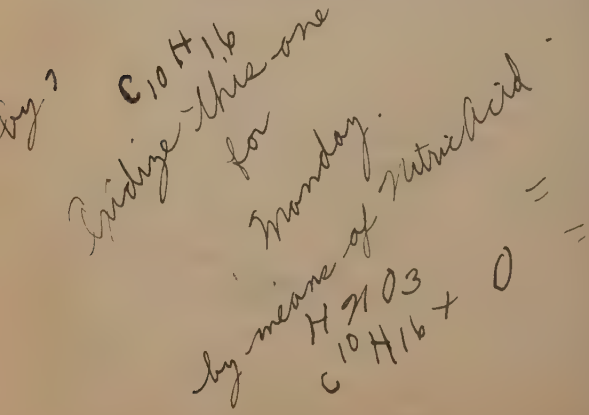
6. If the specific gravity of a sample of nitric acid is 1.522, (*a*) what will 100 cc. weigh, and (*b*) what volume must be taken to weigh 100 gm.?

7. Calculate the simplest formula of the substances having the composition (*a*) O = 76.19, H = 1.58, N = 22.22; (*b*) N = 13.86, K = 38.61, O = 47.52.

8. How many liters of nitrogen and hydrogen are needed to make 800 l. of ammonia gas?

9. What volume of oxygen is needed to combine with the hydrogen obtained by passing electric sparks through 150 cc. of ammonia gas until equilibrium is reached?

10. A solution of ammonium hydroxide contains 14 per cent by weight of the compound $NH_3$. How many liters of the gas $NH_3$ at 100° C. and 748 mm. can be obtained from 150 gm. of the solution?



## CHAPTER XIV

### Atomic and Molecular Weights — Valence

EXTENDED application of atomic and molecular weights has been made in the foregoing pages. In the present chapter we shall consider the methods by which both atomic and molecular weights are determined; several cognate principles of fundamental importance will also be discussed.

**Retrospect.** — Before beginning the development of atomic and molecular weights it will be helpful to review certain facts and assumptions which bear directly upon this subject. It will be recalled that chemical compounds have a definite composition by weight, and furthermore that if the proportions of the elements in a series of compounds containing the same elements are expressed in a special way, the composition is revealed as a simple multiple relation. Again, it will be remembered that gases exhibit a striking similarity of behavior not only when they are subjected to heat and pressure but also when they undergo chemical transformations. These phenomena are summarized in the laws of Boyle, Charles, and Gay-Lussac, which have already been discussed. It has also been seen that in chemical changes neither energy nor matter is lost; transformations occur, but both energy and matter are conserved. Finally we should not forget that the atomic theory offers an acceptable explanation of the composition of matter and of certain aspects of chemical change by assuming that atoms are the gravimetric units of chemical change and by their combinations form molecules which in turn decompose wholly or in part, thereby producing the varied and complicated phenomena succinctly called chemical changes. These atoms have a relative and unvarying

weight called the atomic weight — alike for each atom of the same element, unlike for each atom of different elements. So also each molecule of a compound has a relative and unvarying weight called the molecular weight, which is the sum of the weights of the atoms in one molecule of the compound.

Our present task is to discuss the methods of determining these relative weights of atoms and molecules, and to supplement the data collected in this brief retrospect by certain laws, principles, and theories.

**Determination of Atomic Weights.** — The atomic weight of an element, as already stated, is a relative weight. It is a number expressing the relation of the weight of an atom of a given element to the weight of an atom of some element chosen as a standard. Thus, if we say the atomic weight of nitrogen is 14, we mean that the ratio of the weight of the nitrogen atom and the weight of the hydrogen atom is 14 to 1, provided we adopt 1 as the weight of the hydrogen atom; or we mean that the ratio of the weight of the nitrogen atom and the weight of the oxygen atom is 14 to 16, provided we adopt 16 as the weight of the oxygen atom. Hydrogen was the standard for many years. However, since oxygen combines readily with a large number of elements and forms compounds which are quite suitable for experimental work, the oxygen atom has been adopted as the international standard atom and the weight 16 has been given to it.

When compounds are analyzed, the results show the proportions by weight in which the constituent elements are combined. If one molecule of a compound contained only one atom each of the united elements, the relative weights of the atoms could easily be determined. Thus, approximately 8 parts of oxygen combine with 1 part by weight of hydrogen to form 9 parts of water; assuming that a molecule of water contains only 1 atom of each element, it is

evident that the atomic weight of hydrogen would be 2 if oxygen is 16. But before accepting this conclusion we should not overlook the existence of another compound of hydrogen and oxygen (called hydrogen peroxide) in which 1 part by weight of hydrogen combines with 16 parts of oxygen. Assuming as before that a molecule of hydrogen peroxide contains 1 atom of each element, the conclusion is forced upon us that the atomic weight of hydrogen would be 1 if oxygen is 16. But the atomic weight of hydrogen cannot be both 1 and 2! If we only knew which of the compounds contained a single atom of each element to the molecule, — granting for the time being that such is the case, — the problem would be simple. Analysis does not reveal the number of atoms in a molecule. Obviously additional data are indispensable.

The determination and final selection of the atomic weight of an element is based upon (1) the equivalent weight of the element, (2) the molecular weights of several compounds of the element, and (3) accurate chemical analysis of selected compounds of the element.

**Equivalent Weights.** — The chemical analysis of a compound, as already stated, gives the proportion by weight in which the constituents are combined. If these proportions are stated in a special way instead of the customary form of percentage, certain important relations are revealed. Thus, analysis of ferrous oxide yields approximately 77.77 per cent of iron and 22.22 per cent of oxygen; but if we substitute 8 for 22.22, the weight of iron becomes 28, because 22.22 and 77.77 are in the same ratio as 8 and 28. When a similar process of modification is applied to the percentage of the elements in different compounds, a series of numbers is obtained known as the equivalent weights of the elements. By definition, the **equivalent weight** of an element is the

number of grams which combines with or displaces 8 gm. of oxygen. A partial summary of numerous experiments gives the following: —

TABLE OF EQUIVALENT WEIGHTS

| ELEMENT | EQUIVALENT WEIGHT | ELEMENT | EQUIVALENT WEIGHT |
|---|---|---|---|
| Oxygen . . . . | 8 | Iron (-ous) . | 27.92 |
| Aluminium . . | 9.03 | Iron (-ic) . . | 18.62 |
| Bromine . . . . | 79.92 | Magnesium . | 12.16 |
| Calcium . . . . | 20.05 | Mercury (-ic) | 100 |
| Carbon . . . . | 3 | Potassium . | 39.10 |
| Chlorine . . . . | 35.46 | Silver . . . . | 107.88 |
| Copper (-ous) . | 63.57 | Sodium . . . | 23 |
| Copper (-ic) . . | 31.79 | Sulphur . . . | 16.03 |
| Hydrogen . . . | 1.008 | Zinc . . . . | 32.68 |

This list might be extended to include all the elements which form compounds. These numbers are sometimes called combining numbers, combining weights, or simply equivalents. The term *equivalent weights* is preferable, because they actually are the weights chemically equivalent to each other. Thus, if we start with hydrogen chloride (HCl), 1 gm. of hydrogen — to take a convenient denomination — is combined with 35.46 gm. of chlorine, and this gram of hydrogen can be replaced chemically by 32.68 gm. of zinc, 12.16 gm. of magnesium, 39.10 gm. of potassium, 23 gm. of sodium, and so on. These elements are chemically equivalent in the ratio of these weights.

Equivalent weights are readily found by experiment in most cases. Various methods are used, and the equivalent weight is not always found directly in terms of oxygen. The equivalent of hydrogen is found by passing hydrogen over hot copper oxide — as in the determination of the gravimetric composition of water. The equivalent of magnesium is found by filling a graduated tube with dilute hydrochloric acid, inserting the magnesium, inverting the tube in a dish, and measuring the volume of the liberated hydrogen; knowing the weight of a liter of hydrogen, the weight of the liberated hydrogen

can be calculated, and from its weight the weight of magnesium equivalent to 1 gm. of hydrogen can be found by proportion. The equivalent weight of magnesium can also be found by heating a known weight of magnesium in the air — taking care, of course, not to lose the product. Equivalent weights of copper and other metals as well as of sulphur and of carbon can be found by passing oxygen over these substances in a tube which contains or is attached to a suitable apparatus for retaining the product. The interaction of metals and acids provides a simple method of finding the equivalent of zinc, aluminium, and iron; the interaction of water with sodium and with calcium permits the determination of the equivalent weights of these metals; and the displacement of metals from solutions of their compounds by such metals as zinc and magnesium provides another general method.

Equivalent weights have been very carefully determined by experiment. Comparison of the equivalent weight with the atomic weight of the same element reveals an important relation, as may be seen by the following: —

TABLE OF EQUIVALENT WEIGHTS AND ATOMIC WEIGHTS

| ELEMENT | EQUIVALENT WEIGHT | ATOMIC WEIGHT | MULTIPLE |
|---|---|---|---|
| Oxygen | 8 | 16 | 2 |
| Aluminium | 9.03 | 27.1 | 3 |
| Bromine | 79.92 | 79.92 | 1 |
| Calcium | 20.05 | 40.09 | 2 |
| Carbon | 3 | 12 | 4 |
| Chlorine | 35.46 | 35.46 | 1 |
| Copper (-ous) | 63.57 | 63.57 | 1 |
| Copper (-ic) | 31.79 | 63.57 | 2 |
| Hydrogen | 1.008 | 1.008 | 1 |
| Iron (-ous) | 27.92 | 55.85 | 2 |
| Iron (-ic) | 18.62 | 55.85 | 3 |
| Magnesium | 12.16 | 24.32 | 2 |
| Mercury (-ic) | 100 | 200 | 2 |
| Potassium | 39.10 | 39.10 | 1 |
| Silver | 107.88 | 107.88 | 1 |
| Sodium | 23 | 23 | 1 |
| Sulphur | 16.03 | 32.07 | 2 |
| Zinc | 32.68 | 65.37 | 2 |

An examination of this comparative table shows an integral relation between equivalent weights and atomic weights. In other words, the atomic weight of an element is identical with its equivalent weight or is a simple integral multiple of it. The significance of this relation will be discussed after the subject of molecular weights has been considered.

**Determination of Molecular Weights.** — Before describing the actual methods employed in determining molecular weights, it will be necessary to discuss the kinetic theory of gases and Avogadro's hypothesis. These theoretical principles underlie the interpretation of the results obtained by experiment and assist in the correlation of the properties of gases summarized by the laws of Boyle, Charles, and Gay-Lussac.

**Kinetic Theory of Gases and Avogadro's Hypothesis.** — Extensive study of gases shows that in general they conform to fundamental laws. These laws indicate the uniform and simple structure of all gases. The theory proposed to explain the uniform behavior of gases is called the **kinetic theory.** According to this theory gases are conceived to consist of molecules, moving constantly and rapidly in all directions; these particles are also conceived to have perfect elasticity, and in their movements in the space which is large compared with their own bulk they collide with each other or with the walls of the containing vessel, rebound, and continue to move without loss of energy; furthermore, the molecules of a gas move in straight lines and have little or no tendency to repel or adhere to each other; *i.e.* they are independent particles separated by an average distance much greater than their own diameters. Recasting this theory into a concrete form, a vessel of oxygen gas contains a vast number of molecules, flying about rapidly in the space, striking each other and the walls of the vessel, rebounding

after each collision, some, eventually all, flying out and mingling with the air, but not combining with each other or compressing each other, or even adhering (except under unusual conditions).

Many facts about gases are readily interpreted by this theory. For example, compressibility, diffusion, and the ability to mingle with other gases find explanation in the conception of the constant and rapid motion, perfect elasticity, and relatively great separation of the molecules. Boyle's law finds explanation in the conception of the pressure produced by the incessant impacts of the independent molecules moving in straight lines, the varying pressure being due to the varying number of impacts in a given time produced in the total space within which the gas is confined — the less the space, the greater the pressure. Charles' law is explained by the conception of the change in the velocity of the molecules due to a change in temperature, the uniformly varying volume (at a constant pressure) being due to the varying frequency (and consequently varying energy) of the impacts of the molecules — the more frequent the number of impacts, the greater the pressure in a constant volume, or what is the same thing, the greater the volume at a constant pressure. The law of Gay-Lussac (that is, volumes of combining gases are in a simple integral relation to each other and to the total volume of the gaseous product) must be interpreted jointly by the atomic theory and the kinetic theory. According to the atomic theory chemical union occurs between atoms, while according to the kinetic theory gases consist of molecules. Now, when gases combine, is the combination between atoms or molecules? Let us attempt to answer this question by considering the formation of water by the combination of oxygen and hydrogen gases. According to Gay-Lussac's law two volumes of hydrogen and one volume of oxygen produce two volumes of

water vapor. The simplest assumption (and the one actually made by Dalton when this question was first asked) is that equal volumes of gases contain the same number of atoms. Suppose the number of atoms in a unit volume is X. Then in our illustrative case 2 X atoms of hydrogen unite with X atoms of oxygen to form 2 X atoms of water vapor; *i.e.* each atom of water vapor would contain half an atom of oxygen! But according to the atomic theory there are no fractions of atoms, therefore we must abandon this incorrect assumption that equal volumes of gases contain an equal number of atoms. Another assumption can be made, viz. that equal volumes of gases contain the same number of molecules. This assumption was first made by Avogadro, an Italian physicist, and is still known and accepted in a slightly modified form as Avogadro's hypothesis (see below). If this assumption is made, then the facts summarized by Gay-Lussac's law can be satisfactorily explained. Let the number of molecules in a given volume of a gas be Z. Applying our assumption to the previous illustration, 2 Z molecules of hydrogen combine with Z molecules of oxygen to form 2 Z molecules of water vapor. Now a molecule of hydrogen and of oxygen each consists of at least two atoms (as will soon be shown). Therefore the illustration can be interpreted as follows: The given volume contains Z molecules. The 2 Z volumes of hydrogen contain 2 Z molecules or 4 Z atoms, while the Z volume of oxygen contains Z molecules or 2 Z atoms; or 6 Z atoms all together. When these volumes unite, 2 volumes of water vapor are formed which contain 2 Z molecules of water vapor. Now if we assume temporarily the fact that a molecule of water vapor consists of 2 atoms of hydrogen and 1 of oxygen, it is obvious that not only are the requisite number of atoms available to form 2 molecules of water vapor, but that exactly 2 molecules must be formed. In a few words, if we accept the view that gaseous particles

are not atoms but molecules, then Avogadro's hypothesis follows as a logical conclusion.

**Avogadro's hypothesis** is usually stated thus: —

*There is the same number of molecules in equal volumes of all gases at a given temperature and pressure.*

This hypothesis means, for example, that a liter of hydrogen and a liter of oxygen at the same temperature and pressure contain the same number of molecules. It therefore follows that the weights of single molecules in equal volumes of these two gases (and all other gases) at a given temperature and pressure are in the same ratio as the weights of their equal volumes. Hence to find the relative weights of gaseous molecules, it is only necessary to determine and compare the actual weights of equal volumes of the gases at a given temperature and pressure. Furthermore, if we express the weights of molecules in terms of the standard adopted for atomic weights, we have found the molecular weight of the substance. It is clear, then, that the molecular weights of elements and compounds in the gaseous state can be found by (1) assuming the kinetic theory and Avogadro's hypothesis, and (2) determining experimentally the relative weights of gases.

The hypothesis of Avogadro was proposed in 1811. But it was not favorably received nor was it utilized in finding molecular weights until about 1858. At this time it was shown by Cannizzaro, a countryman of Avogadro, to be a reliable hypothesis, since its application yielded molecular weights in almost complete agreement with the weights found by other methods. Or more strictly, the atomic weights of the elements derived by all methods (including the method which involved Avogadro's hypothesis) were uniform, accurate, and on a consistent theoretical basis. Although this hypothesis cannot be proved by the methods usually used in chemical investigations and can never have the certainty of a demonstrable law, it has been tested in many ways and is accepted as an established principle; no facts are known which are not in harmony with it.

**Determination of Molecular Weights by the Vapor Density Method.** — The density of a gas or vapor is its relative weight, *i.e.* its weight in terms of a standard. Thus, if the density of hydrogen is accepted as 1, the density of oxygen is about 16, because a given volume of oxygen weighs about sixteen times as much as an equal volume of hydrogen at the same temperature and pressure. Similarly, if the density of air is accepted as 1, the density of oxygen is about 1.1 because the weights of equal volumes under the same conditions are in this ratio. We may, however, choose any standard, such as hydrogen = 2 or oxygen = 32, since the different values can be readily transformed into each other when we know the numerical relation of the standards.

For many years hydrogen was the standard gas for expressing vapor density, and the molecular weights of gases and vapors were found by multiplying their vapor densities by 2, thus: —

Molecular Weight = Vapor Density referred to Hydrogen × 2.

The vapor density is multiplied by 2 because the molecular weight of hydrogen is 2; and the molecular weight of hydrogen is 2 because a molecule of hydrogen contains at least two atoms each having the atomic weight 1. The conclusion that the hydrogen molecule contains at least two atoms is based on the following: —

One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride (HCl). Suppose the volume of hydrogen contains 1000 molecules. Then, according to Avogadro's hypothesis, the equal volume of chlorine will contain 1000 molecules, while the two volumes of the product will contain 2000 molecules of hydrogen chloride. That is: —

1000 molecules of Hydrogen + 1000 molecules of Chlorine
= 2000 molecules of Hydrogen Chloride.

Now since every molecule of hydrogen chloride contains at least one atom each of hydrogen and chlorine, the 2000 molecules must contain at least 2000 atoms each of hydrogen and chlorine. But the 2000 atoms of hydrogen and of chlorine were provided by the 1000 molecules of hydrogen and the 1000 molecules of chlorine. Therefore each molecule of hydrogen and of chlorine must contain at least two atoms. There is no evidence which leads us to believe that the chlorine or the hydrogen molecule contains more than two atoms. That is, no case is known in which a given volume of hydrogen gas furnishes the material for more than two volumes of the gaseous product; the same is true of chlorine. On this ground we base our belief that every hydrogen and every chlorine molecule contains only two atoms.

There are good reasons, however, for adopting oxygen gas = 32 as the standard for expressing vapor density. The atomic weight of oxygen is 16, and this is the international standard for atomic weights. Hence if we express molecular weights in terms of the atomic weight of oxygen, these values then become a consistent part of the international system of expressing the quantitative aspects of chemical change. The molecular weight of oxygen is 32, because a molecule of oxygen contains two atoms. This conclusion is based on the following: —

Two volumes of hydrogen unite with one volume of oxygen to form two volumes of water vapor. Suppose a single volume contains 1000 molecules. Then the two volumes of water vapor must contain 2000 molecules and each molecule must contain at least one atom of oxygen, or 2000 atoms of oxygen in all. Since 2000 atoms of oxygen were furnished by the 1000 molecules of oxygen, each molecule of oxygen must contain at least two atoms; and no facts lead us to believe that there are more than two atoms.

As the atomic weight of oxygen is 16, the molecular weight is 32.

The general method of determining the molecular weight of a substance by the vapor density method is now clear. It is only necessary to determine by experiment the weight of a known volume of the gas or vapor on the oxygen basis and then multiply this weight by 32. That is: —

Molecular Weight = Vapor Density referred to Oxygen × 32

For example, a liter of carbon dioxide gas weighs about 1.38 times as much as a liter of oxygen (*i.e.* 1.977 ÷ 1.429 = 1.38). Therefore 1.38 is the vapor density of carbon dioxide referred to oxygen, and the molecular weight is 1.38 × 32, or about 44.

**Experimental Determination of Molecular Weights.** — The weight of one liter of oxygen has been carefully determined. Hence the simplest method of determining the molecular weight of a gas or vapor would appear to be merely to find the exact weight of a liter of the gaseous or vaporized substance and then refer this to the standard. It is more convenient experimentally, however, to find the volume of air displaced by the vapor of a known weight of a substance. An example will make this method clear. The vapor from .1008 gm. of chloroform displaced 22 cc. of air at 16.5° C. and 707.5 mm. The corrected volume of air is 18.93 cc. That is, .1008 gm. of dry chloroform, if at 0° C. and 760 mm., would occupy 18.93 cc. The weight of a liter is found by the following proportion: —

$$18.93 : 1000 : : .1008 : x$$

$x = 5.324$. Therefore the vapor density equals 5.324 ÷ 1.429, or 3.6557; and the molecular weight equals 3.6557 × 32, or 117. The exact molecular weight of chloroform vapor is 119.5.

A vapor density method frequently used is one devised by Victor Meyer. A simplified form of the apparatus is shown in Figure 26. The bulb *B* of the inner tube is heated to a constant temperature by the vapor of the liquid boiling in the larger tube *A*. The gas measuring tube *D*, filled with water, is then inverted in the vessel of water *E* over the end of the capillary tube *C*. Finally, a weighed quantity of the substance (in a small bulb or bottle) is introduced into *B* by quickly removing and replacing the stopper *F*; a wad of glass wool or asbestos at the bottom of *B* prevents the tube from being broken. The substance soon vaporizes, and the vapor forces its own volume of air into the gas tube *E*. When the substance is completely vaporized, the volume of air in *D* is measured and reduced to the volume it would occupy if it were a dry gas at 0° C. and 760 mm. The corrected volume is the volume of the known weight of the substance.

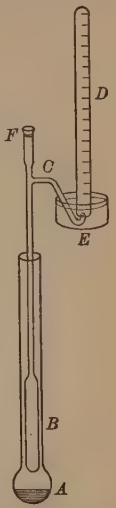



FIG. 26. — Apparatus for determining vapor density.

The vapor density method is limited, of course, to those substances that are gaseous or can be vaporized without decomposition. For many years it was the only reliable method of finding molecular weights. Two other methods are now available which are susceptible of wider application; viz. the freezing point and the boiling point methods.

In Chapter IX it was stated that the freezing point of a solution is lower than the freezing point of the solvent, and that the depression of the freezing point in dilute solutions is approximately proportional to the concentration of the solution in the case of all substances which are not ionized or do not unite with the solvent. Furthermore, by extending the results obtained by experiments with dilute solutions, it has been found that if a mole (*i.e.* a number of grams numerically equal to the molecular weight) of substances which

depress the freezing point normally is dissolved in 1000 gm. of water, the freezing point of all such solutions is depressed the same number of degrees; *i.e.* each solution freezes at approximately $-1.89°$ C. This means, for example, that a solution of 342 gm. of sugar ($C_{12}H_{22}O_{11}$) in 1000 gm. of water freezes at approximately $-1.89°$ C. Since this number ($-1.89$) is the same for all solutions containing the molecular weight in grams in 1000 gm. of water, it is sometimes called the molecular depression constant (K). Now, if we find by experiment the amount of depression of the freezing point caused by a solution of known concentration, the molecular weight of the solute is readily calculated. An example will make this point clear. It was found that a solution of 50 gm. of methyl alcohol in 1000 gm. of water froze at approximately $-2.95°$ C. A solution containing one mole (*i.e.* a gram-molecular weight) of methyl alcohol in 1000 gm. of water would freeze at approximately $-1.89°$ C. Hence the molecular weight in grams is found by the proportion —

$$50 : x : : -2.95 : -1.89$$

or $x = 32$. That is, 32 is the molecular weight of methyl alcohol.

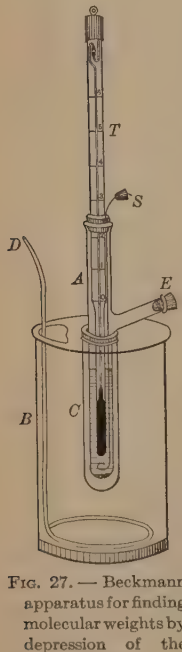



FIG. 27. — Beckmann apparatus for finding molecular weights by depression of the freezing point.

This method of finding molecular weights was first applied extensively by Raoult (1830–1901) and is sometimes called the cryoscopic method. The experiment may be performed in an apparatus devised by Beckmann (Fig. 27). The solvent is placed in the inner tube *A* provided with a side tube *E* through which the solute is introduced. A very accurate and delicate ther-

mometer $T$ passes through a stopper into the inner tube, which is also provided with a stirrer $S$. An outer tube $C$ serves as an air jacket, and is surrounded by the freezing mixture, which is placed in the large vessel $B$. A weighed quantity of the solvent is put into the tube $A$, and its freezing point is carefully determined. Then a weighed quantity of the solute is introduced through the side tube $E$, and the freezing point of the solution is determined. The difference between the two freezing points is the depression, and from this depression the molecular weight can be calculated. Let us take an example. Suppose 4.98 gm. of sugar ($C_{12}H_{22}O_{11}$) are dissolved in 96.9 gm. of water and the depression is .287° C. Since 96.9 gm. of water contain 4.98 gm. of sugar, 1000 gm. of water would contain 51.39 gm. of sugar. If 51.39 gm. of sugar cause a depression of .287°, then the number of grams which would cause the molecular depression can be found by the proportion —

$$51.39 : .287 :: x : 1.89,$$

or $x = 338$. The correct value is 342.

Molecular weights can also be determined by an analogous method known as the boiling-point method.

**Exact and Approximate Molecular Weights.** — All experimental methods yield results which agree closely. The molecular weights found by experiment, however, are not exactly equal to the molecular weights found by adding the weights of the atoms in one molecule. Thus, in the case just cited there is a difference of 4 between the experimental and the accepted molecular weight of sugar. The difference in this and similar cases is due partly to the difficulties in making accurate measurements of temperature, partly to impurities in the substances and slight defects in the experimental method, and partly also to the erroneous assumption that Avogadro's hypothesis is absolutely true for all temperatures. The errors are slight and do not affect the validity of the general result. Most molecular weights used in chemical discussions and calculations are calculated molecular weights. That is, after the composition of the substance has been

determined by analysis, the molecular weight found by experiment is slightly changed so that it will equal the sum of the weights of the atoms in a single molecule. It should be noted that the failure to find exact molecular weights by experiment is not a serious misfortune. The goal is atomic weights, and if these are accurately determined (as they can be), the exact molecular weight is readily found by merely adding the atomic weights corresponding to the number of atoms in the molecule. But, as repeatedly stated, approximate molecular weights must be known in order to find the atomic weights of the elements. It should be noted further that the methods of finding molecular weights described in the foregoing pages apply only to substances in the gaseous or dissolved state. No experimental method is known for determining the molecular weights of substances in the solid state. Therefore, unless there is evidence to the contrary, the molecular weight of a substance in the solid state is assumed to have the same value as that found by the usual methods.

**Relation of Atomic Weights to Molecular Weights and Equivalent Weights and Determination of Atomic Weights.** — It has been shown that the atomic weights of the elements bear a simple numerical relation to molecular weights and equivalent weights. Furthermore, the methods of determining and calculating both molecular and equivalent weights have been described. It is now appropriate to discuss the methods of selecting that weight known as the atomic weight, which bears the correct relation to the equivalent weight on the one hand and the molecular weight on the other.

The first method we shall consider is known as the **highest common factor method.** It consists in finding by appropriate chemical and physical methods (*a*) the molecular

weights of several representative compounds of the element, (*b*) the weight of the element contained in that number of grams numerically equal to the molecular weight, and then (*c*) calculating the highest common factor of the weights found in (*b*). This procedure applied to the element carbon can be tabulated as follows: —

| Substance | Molecular Weight | Weight of Carbon in Gram-molecular Weight |
|---|---|---|
| Carbon Monoxide | 28 | 12 |
| Carbon Dioxide | 44 | 12 |
| Carbon Disulphide | 76 | 12 |
| Methane | 16 | 12 |
| Ethylene | 28 | 24 |
| Ether | 74 | 48 |
| Acetylene | 26 | 24 |
| Acetic Acid | 60 | 24 |

The highest common factor of the numbers in the second column is 12. That is, the smallest weight of carbon in a molecule of these representative carbon compounds is 12. In other words, the atomic weight of carbon is 12. Another case will make this method still clearer. Proceeding as above with the element oxygen, we have the following table: —

| Substance | Molecular Weight | Weight of Oxygen in Gram-molecular Weight |
|---|---|---|
| Oxygen | 32 | 32 |
| Ozone | 48 | 48 |
| Water | 18 | 16 |
| Ether | 74 | 16 |
| Acetic Acid | 60 | 32 |

The highest common factor of the numbers in the last column is 16, and since this is the smallest weight of oxygen in a molecule of its compounds, this number (16) is selected as the atomic weight of oxygen.

A comparison of the atomic weights of carbon and oxygen with their equivalent weights reveals the following relations:—

| Element | Atomic Weight | Equivalent Weight | Multiple |
|---|---|---|---|
| Carbon | 12 | 3 | 4 |
| Oxygen | 16 | 8 | 2 |

Similar relations exist between the equivalent weights and atomic weights of all the elements. That is, the atomic weight of an element is equal to the equivalent weight or to a small integral multiple of it. (See table on p. 231.) This relation now demands a fuller explanation than hitherto given. The equivalent weight, as previously stated, is a number obtained by expressing in a special way the per cent in which elements combine or exchange places. It is simply the number of parts by weight of an element which combine with or displace 8 parts by weight of oxygen. But the equivalent weight is not the unit used in chemistry to express the composition of compounds or the quantitative relations of the elements. The atomic weight is the quantitative unit. Hence the equivalent weights must be multiplied by those integers which will transform the equivalent weight into the atomic weight. That is to say, the equivalent weights are the fundamental empirical proportions, while the atomic weights are the adjusted gravimetric units deduced from the equivalent weights on the one hand and from the molecular weights on the other hand so as to har-

monize the atomic weights with the system adopted in chemistry for expressing those relations of the elements which have been established not only by facts, but also by certain accepted theories.

The atomic weights determined by the highest common factor method are only approximate, but they serve as a basis for the selection of the atomic weights. That is, we find by this method that the atomic weight of chlorine, for example, is not a multiple or submultiple of 35.5, and, moreover, that the value is very nearly 35.5. The same conclusion can be drawn regarding the atomic weight of any element to which the highest common factor method is applicable.

Another method for determining atomic weights, applicable to the solid elements only, is known as **Dulong and Petit's method** because it utilizes an approximate law announced and applied by them about 1819. The law, commonly called the **law of specific heats**, may be stated as follows: —

*The product of the specific heat and atomic weight of the solid elements is approximately equal to* 6.25.

By specific heat is meant the quantity of heat necessary to raise the temperature of a substance one degree compared with the quantity necessary to raise the temperature of the same weight of water one degree. If the same quantity of heat is imparted to equal weights of water and mercury, the temperature of the mercury will be much higher — about 32 times higher than that of the water. That is, the mercury requires only about $\frac{1}{32}$ as much heat as the water. In other words, the specific heat of mercury is $\frac{1}{32}$, or .0312. The specific heat of elements in the solid state can be found readily by experimental methods. The number found by multiplying the specific heat of a solid element by its atomic weight varies somewhat, but in many cases it is between

6 and 6.5 (approximately 6.25). This relation is illustrated by the following: —

TABLE OF SPECIFIC HEATS

| ELEMENT | SPECIFIC HEAT | APPROXIMATE ATOMIC WEIGHT | PRODUCT |
|---|---|---|---|
| Calcium | .170 | 40 | 6.8 |
| Copper | .095 | 63.5 | 6.03 |
| Iron | .114 | 56 | 6.38 |
| Lead | .031 | 207 | 6.41 |
| Potassium | .166 | 39 | 6.47 |
| Sodium | .293 | 23 | 6.73 |
| Sulphur | .178 | 32 | 5.7 |
| Tin | .055 | 119 | 6.54 |
| Zinc | .094 | 65.5 | 6.15 |

Dulong and Petit's law is only an approximation, and it serves merely to check values obtained by other methods and to show whether the atomic weight of an element is a multiple of the equivalent, or identical with it. The use of the law in checking atomic weights may be illustrated as follows: The specific heat of silver was found to be .057; if 6.25 is divided by this number, the quotient is about 109. This result shows that the atomic weight of silver is certainly not 55 or 218, but is approximately 109 (the exact value being 107.88). Again, the atomic weight of uranium may be 238 or 119 according to the chemical analysis; but only the former conforms to Dulong and Petit's law, and hence it is accepted as the approximate atomic weight.

When the approximate atomic weight of an element has been chosen on the basis of the foregoing principles, the task still remains to determine the accurate value of this important weight by **chemical analysis.** The general method employed can be illustrated by a determination made by the Belgian chemist, Stas, whose work was very accurate. He

found that 121.4993 gm. of silver chloride were formed by burning 91.462 gm. of silver in chlorine. He accepted AgCl as the formula of silver chloride and 35.453 as the atomic weight of chlorine, and calculated the atomic weight of silver thus : —

$$121.4993 - 91.462 = 30.0373$$

Wt. of silver : Wt. of chlorine : : At. wt. of silver : At. wt. of chlorine

$$91.462 : 30.0373 :: x : 35.453$$

$$x = 107.95$$

The exact value now accepted is 107.88. The atomic weights of many elements are determined by analogous analytical methods.

The exact determination of atomic weights is a difficult task. And although the utmost care is used in purifying the chemicals and performing the analysis, the results of different experimenters do not always exactly agree. Therefore an international committee was chosen several years ago to select the most accurate atomic weights of the elements. These weights are embodied in a table published annually and called the International Table of Atomic Weights. The entire table is given in the Appendix, § 5, and a supplementary table is given on the inside of the back cover. In the latter table the accepted atomic weights are placed in one column and the approximate values in another. The approximate atomic weights are often sufficiently accurate for general reference and in making chemical calculations; they may be used in solving the problems in this book.

The methods and principles used in determining the atomic weight of an element can be reviewed by the general plan which would be followed out in the case of zinc (if its atomic weight were unknown). (*a*) The equivalent of zinc is found by experiment to be 32.5. Therefore the atomic weight is 32.5, or some multiple of this number.

(*b*) The molecular weight of zinc chloride is found by its vapor density to be 135. (*c*) Analysis of zinc chloride yields 47.8 per cent of zinc. Therefore, 47.8 per cent of 135, or 64.5, is zinc. That is, this number 64.5 is the weight of the smallest part of zinc in zinc chloride, and it may be the weight of one atom. (*d*) The specific heat of zinc is about .094. Applying Dulong and Petit's law, the approximate atomic weight is found to be 66.4 (*i.e.* $6.25 \div .094$). Therefore, the atomic weight is about 65, and not 32.5. (*e*) Careful analysis of zinc compounds shows that the atomic weight of zinc (on the basis $O = 16$) is 65.37.

**Determination of Formulas of Compounds.** — The formula of a compound is an expression of its composition; that is, it is a group of symbols which not only expresses the proportions of the weights of the elements in a compound, but also the number of atoms whose sum equals the molecular weight. In a word, a formula is a molecular formula, provided, of course, the molecular weight is known. For example, the proportion of hydrogen to chlorine in hydrogen chloride is 1 to 35.5, and the molecular weight is known to be 36.5; therefore, there must be one atom each of hydrogen and chlorine in a molecule, and the formula is HCl.

Again, the proportion of carbon to hydrogen in a certain hydrocarbon is 12 to 2, and its vapor density (referred to oxygen) is 5.09. The formula would be $CH_2$ according to the proportions by weight. But the molecular weight of such a compound would be only 14 (*i.e.* $12 + 2$), whereas the vapor density of the original hydrocarbon necessitates the molecular weight 162.88 (*i.e.* $32 \times 5.09$), which is nearly twelve times the weight corresponding to $CH_2$. Hence the molecular formula is not $CH_2$, but $C_{12}H_{24}$. Again, the proportion of hydrogen to oxygen in hydrogen peroxide is 1 to 16, and the formula HO would express this proportion. But the molecular weight of hydrogen peroxide has been found by the freezing point method to be nearly 34. Therefore, $H_2O_2$, not HO, must be the formula, because $H_2O_2$ corre-

sponds to the molecular weight as well as to the proportions by weight.

If the composition of a compound is known, the smallest number of atoms corresponding to the composition can be readily calculated by dividing the per cent of each element in the compound by the atomic weight (and, if necessary, reducing the quotients to the smallest whole numbers). That is, we merely transform the percentage into numbers which express the atomic relations by distributing the proportional parts among the elements according to that method of expressing composition adopted in chemistry. Some examples will make this point clear. According to analysis, a compound contains 40 per cent of calcium, 12 per cent of carbon, and 48 per cent of oxygen. Dividing each per cent by the proper atomic weight, we have : —

$$40 \div 40 = 1$$
$$12 \div 12 = 1$$
$$48 \div 16 = 3$$

That is, one molecule of this compound contains (at least) one atom each of calcium and carbon, and three atoms of oxygen. Hence, the simplest formula is $CaCO_3$. Again, a compound was found to contain 2.04 per cent of hydrogen, 32.65 per cent of sulphur, and 65.31 per cent of oxygen. Proceeding as in the previous case, we have : —

$$2.04 \div 1 = 2.04$$
$$32.65 \div 32 = 1.02$$
$$65.31 \div 16 = 4.08$$

Reducing these quotients to the smallest set of integral numbers, we have : —

$$2.04 \div 1.02 = 2$$
$$1.02 \div 1.02 = 1$$
$$4.08 \div 1.02 = 4$$

That is, one molecule of this compound contains two atoms of hydrogen, one of sulphur, and four of oxygen. Hence the simplest formula is $H_2SO_4$. If the molecular weight of a compound cannot be found, then the simplest formula (found as in the above cases) is usually accepted as the molecular formula. Finally, a compound was found by analysis to contain 92.3 per cent of carbon and 7.7 per cent of hydrogen; the vapor density (referred to oxygen) was 2.4375. Proceeding as above, we have: —

$$92.3 \div 12 = 7.7 \text{ or } 1$$
$$7.7 \div 1 = 7.7 \text{ or } 1$$

That is, the compound contains at least one atom of carbon and hydrogen, and would have the formula CH, if nothing were known about its molecular weight. The vapor density 2.4375 requires the molecular weight 78, which is six times the weight (13) corresponding to the formula CH. Hence the correct formula of this compound is not CH but $C_6H_6$.

To recapitulate: The simplest formula of a compound is found by dividing the per cent of each element by its atomic weight and reducing these quotients to the smallest whole numbers (if necessary); if the molecular weight is not known, this formula is accepted as the molecular formula. The molecular formula of a compound is found by three steps: (*a*) Find the simplest formula, (*b*) divide the molecular weight by the sum of the weights of the atoms in the simplest formula, (*c*) multiply the integral numbers of the simplest formula by the quotient obtained in (*b*). (Compare illustration in preceding paragraph.)

**Molecular Formulas of Gases and Vapors.** — Gaseous or vaporized elements are in the molecular state (with a few exceptions), and the number of atoms in the molecule varies in different elements. **Thus,** hydrogen, oxygen, chlorine,

and nitrogen have two atoms to the molecule, and the formulas of their molecules are respectively $H_2$, $O_2$, $Cl_2$, $N_2$. Ozone has the formula $O_3$. The molecular formula of several elements varies with the temperature. Sulphur vapor has the formula $S_2$ or $S_8$ and phosphorus $P_2$ or $P_4$ according to the temperature. Cadmium, mercury, potassium, sodium, and zinc vapors have only one atom to the molecule, and the formulas of these elementary vapors are respectively Cd, Hg, K, Na, and Zn. To be consistent, therefore, the formulas $H_2$, $O_2$, $Cl_2$, $N_2$, etc., should be used for these (and other diatomic) gases when we wish to represent free and uncombined elements. Similarly, the element argon, which is a monatomic gas, should be represented by A, and ozone, which is triatomic, by $O_3$. The formulas of elements in the state of vapor should also be similarly written, *e.g.* Zn, $S_2$ or $S_8$, $P_2$ or $P_4$. However, elements like zinc, sulphur, phosphorus, and carbon, which are solids or are usually used in the solid state, are more often represented by symbols, *e.g.* Zn, 2 S, 3 C, 4 P. In the preceding chapters symbols have been uniformly employed for gases, *e.g.* H, 2 O, 3 Cl, etc. In subsequent chapters, now that molecular formulas have been discussed, gases will be represented by molecular formulas unless, of course, the atomic formula is demanded by the conditions of the experiment.

Since reactions between gases are between molecules, equations representing such reactions should be written in the molecular form. For example, the **molecular equation** for the formation of water vapor from hydrogen and oxygen is —

$$2\,H_2 + O_2 = 2\,H_2O$$

It is read thus: Two molecules of hydrogen unite with one molecule of oxygen to form two molecules of water vapor. Since most elementary gases consist of molecules, such equations correctly represent the actual substances in-

volved. It should be noted, however, that the proportions by weight are the same as in the simpler or atomic form of the equation. Molecular equations are sometimes called **volume equations** or **gas equations**, because they show the volumes involved in the reaction. Thus, the equation

$$H_2 + Cl_2 = 2\,HCl$$

means that one volume each of hydrogen and chlorine unite to form two volumes of hydrogen chloride, or more fully the equation is —

$$\underset{1\text{ vol.}}{H_2} + \underset{1\text{ vol.}}{Cl_2} = \underset{2\text{ vols.}}{2\,HCl}$$

## Valence

A classification of the formulas of chemical compounds shows certain regularities. Instead of a vast number of unrelated formulas, there are really only a few groups, especially if attention is confined to inorganic compounds. Take, for instance, some binary compounds of hydrogen. They fall into the following classes: —

| | | | |
|---|---|---|---|
| $HCl$ | $H_2O$ | $NH_3$ | $CH_4$ |
| $HBr$ | $H_2S$ | $PH_3$ | $SiH_4$ |
| $HI$ | | $AsH_3$ | |
| $HF$ | | $SbH_3$ | |

Again, if some oxides are considered, we have the following: —

| | | | | | | |
|---|---|---|---|---|---|---|
| $Na_2O$ | $CuO$ | $Al_2O_3$ | $MnO_2$ | $P_2O_5$ | $SO_3$ | $I_2O_5$ |
| $K_2O$ | $MgO$ | $P_2O_3$ | $SO_2$ | $As_2O_5$ | $CrO_3$ | |
| $Ag_2O$ | $CaO$ | $As_2O_3$ | $CO_2$ | | | |

We might also group certain acids and salts thus: —

| | | | |
|---|---|---|---|
| $HCl$ | $H_2SO_4$ | $HNO_3$ | $H_3PO_4$ |
| $NaCl$ | $Na_2SO_4$ | $NaNO_3$ | $Na_3PO_4$ |
| $CaCl_2$ | $CaSO_4$ | $Ca(NO_3)_2$ | $Ca_3(PO_4)_2$ |
| $AlCl_3$ | $Al_2(SO_4)_3$ | $Bi(NO_3)_3$ | $Mg_3(PO_4)_2$ |

Similarly, there are the following groups of bases: —

| | | |
|---|---|---|
| $NaOH$ | $Ca(OH)_2$ | $Al(OH)_3$ |
| $KOH$ | $Ba(OH)_2$ | $Bi(OH)_3$ |

If these lists were to be extended, similar regularities would be revealed. A careful examination of these formulas leads to two conclusions. (1) Atoms of elements differ in the number of atoms or atomic groups of the other elements with which they combine. Thus, in the first list one atom each of chlorine, bromine, iodine, and fluorine combines with one atom of hydrogen; one atom of oxygen and of sulphur combines with two of hydrogen; and so on through all the lists. (2) An atom of certain elements always unites with only one atom of certain other elements, with only two atoms of certain others, and so on. That is, if the elements were properly classified, they would exhibit a maximum numerical combining capacity, so to speak.

It must be concluded from an extensive study of chemical change that atoms of the elements are endowed, as it were, with a definite and characteristic combining capacity. The number which expresses the maximum combining capacity of an atom of an element is called the **valence** of the element.

**Determination of Valence.** — The valence of an element is found by dividing the atomic weight by the equivalent weight. It will be recalled that elements combine in the ratio of their equivalent weights. That is, if the per cent of each element in a compound is restated so that these per cents become the number of grams which unites with or replaces eight grams of oxygen, the composition of the compound is expressed in terms of the equivalent weights of the constituent elements. For example, magnesium and oxygen combine in the ratio of 60 and 40 per cent respectively (in round numbers). If for the 40 per cent we substi-

tute 8, then the 60 per cent becomes 12, *i.e.* the equivalents of oxygen and magnesium respectively. We have seen, however, that atomic weights, not equivalent weights, are the weights used in chemistry for expressing composition. The number, therefore, which expresses the maximum combining capacity of an atom of an element is merely the factor by which the equivalent weight is multiplied to convert it into the atomic weight. To find the valence, it is only necessary to divide the atomic weight by the equivalent weight. In brief,

$$\text{Valence} = \frac{\text{Atomic Weight}}{\text{Equivalent Weight}}$$

Pursuing this method of finding valence, we obtain the following: —

A. Table of Valence of Common Elements

| Element | Symbol | Valence |
|---|---|---|
| Aluminium | Al | III |
| Ammonium | $NH_4$ | I |
| Antimony | Sb | III in antimonous and V in antimonic compounds |
| Arsenic | As | III in arsenious and V in arsenic compounds |
| Barium | Ba | II |
| Bismuth | Bi | III |
| Boron | B | III |
| Bromine | Br | I in hydrobromic acid (HBr) and bromides |
| Cadmium | Cd | II |
| Calcium | Ca | II |
| Carbon | C | IV |
| Chlorine | Cl | I in HCl and chlorides; V in chlorates |
| Chromium | Cr | III; VI in chromates and dichromates |
| Cobalt | Co | II |
| Copper | Cu | I in cuprous and II in cupric compounds |
| Fluorine | F | I |
| Gold | Au | I in aurous and III in auric compounds |
| Hydrogen | H | I |

A. TABLE OF VALENCE OF COMMON ELEMENTS — *Continued*

| ELEMENT | SYMBOL | VALENCE |
|---|---|---|
| Iodine . . . | I | I in hydriodic acid (HI) and iodides |
| Iron . . . | Fe | II in ferrous and III in ferric compounds |
| Lead . . . | Pb | II; IV in $PbO_2$ |
| Lithium . . | Li | I |
| Magnesium . | Mg | II |
| Manganese . | Mn | II; IV in $MnO_2$; VI in manganates; VII in permanganates |
| Mercury . . | Hg | I in mercurous and II in mercuric compounds |
| Nickel . . . | Ni | II |
| Nitrogen . . | N | I in $N_2O$; III in $N_2O_3$ and nitrites; V in $N_2O_5$, $HNO_3$, and nitrates |
| Oxygen . . | O | II |
| Phosphorus . | P | III in $P_2O_3$; V in $P_2O_5$, $H_3PO_4$, and orthophosphates |
| Platinum . . | Pt | IV |
| Potassium . | K | I |
| Silicon . . . | Si | IV |
| Silver . . . | Ag | I |
| Sodium . . | Na | I |
| Strontium . | Sr | II |
| Sulphur . . | S | II in $H_2S$ and sulphides; VI in $SO_3$, $H_2SO_4$, and sulphates |
| Tin . . . . | Sn | II in stannous and IV in stannic compounds |
| Zinc . . . . | Zn | II |

Strictly speaking, the conception of valence is applicable only to elements. But many groups of atoms of different elements often act chemically like individual atoms of elements (*i.e.* they pass as a whole from compound to compound); hence it is customary to assign a valence to atomic groups like $SO_4$, $NO_3$, etc. These groups are often called radicals, and are analogous to $NH_4$ and OH. Tabulating the common radicals and a few elements, we have: —

B. Table of Valence of Certain Elements and Radicals

| Chemical Name of Compound which contains Element or Radical | Symbol or Formula | Valence |
|---|---|---|
| Acetate | $C_2H_3O_2$ | I |
| Bromide | Br | I |
| Carbonate (normal) | $CO_3$ | II |
| Carbonate (acid) | $HCO_3$ | I |
| Chlorate | $ClO_3$ | I |
| Chloride | Cl | I |
| Chromate | $CrO_4$ | II |
| Cyanide | CN | I |
| Dichromate | $Cr_2O_7$ | II |
| Fluoride | F | I |
| Hydroxide | OH | I |
| Iodide | I | I |
| Manganate | $MnO_4$ | II |
| Nitrate | $NO_3$ | I |
| Nitrite | $NO_2$ | I |
| Permanganate | $MnO_4$ | I |
| Phosphate (ortho) | $PO_4$ | III |
| Silicate | $SiO_3$ | II |
| Sulphate | $SO_4$ | II |
| Sulphide | S | II |
| Sulphite (normal) | $SO_3$ | II |
| Sulphite (acid) | $HSO_3$ | I |

Both tables are indispensable in writing formulas, as will be shown below.

It is obvious from these tables that the valence of an element is not the same under all circumstances. Many, to be sure, have a fixed valence, but several of the common elements, such as sulphur and nitrogen, have a valence which is doubtless determined by the element with which they are united and the conditions under which the union occurred. The valence of an element is never less than 1 nor more than 8. The valence of most radicals is fixed.

Elements and groups which have the valence I are called monads or univalent elements ; those which have the valence II are called dyads or bivalent elements; similarly, those elements or groups which have the valence III, IV, V, VI, and VII are called respectively triads, tetrads, pentads, hexads, and heptads ; the corresponding adjectives are trivalent, quadrivalent, quinquivalent, hexavalent, and heptavalent.

Elements which have the same valence combine with each other atom for atom. Thus, one atom of sodium combines with one atom of chlorine to form one molecule of sodium chloride ; one atom of magnesium combines with one atom of oxygen to form one molecule of magnesium oxide. Elements having a different valence usually combine with each other so that the total valence of the atoms of each element in a molecule is equal, *i.e.* in many compounds the total combining capacity of each element is equal. This condition is often described by calling the compound saturated, or as one having a balanced valence. Thus, two atoms of hydrogen combine with one of oxygen to form one molecule of water ($H_2O$); two atoms of aluminium each having the valence III combine with three atoms of oxygen each having the valence II to form one molecule of aluminium oxide ($Al_2O_3$); one atom of carbon having the valence IV combines with two atoms of sulphur each having the valence II to form one molecule of carbon disulphide ($CS_2$). The same rules apply to atomic groups. Thus, one $NH_4$-group combines with one OH-group to form one molecule of ammonium hydroxide ($NH_4OH$); two $NH_4$-groups combine with one $SO_4$-group having the valence II to form one molecule of ammonium sulphate ($(NH_4)_2SO_4$); and three atoms of calcium each having the valence II combine with two $PO_4$-groups each having the valence III to form one molecule of calcium phosphate ($Ca_3(PO_4)_2$).

It is convenient to interpret valence not only from the standpoint of combination, but also from the standpoint of displacement. That is, just as atoms and groups of the same valence combine unit for unit, or those of different valence combine so that the valences of each element or atomic group balance, so also atoms and atomic groups displace each other — unit for unit if the valence is the same, or equivalently if the valence is different. For example, when zinc displaces hydrogen in hydrochloric acid, one atom of zinc having the valence II displaces two atoms of hydrogen each having the valence I, and the formula of the resulting zinc chloride is $ZnCl_2$; similarly, one atom of sodium having the valence I displaces one atom of hydrogen from water, and the formula of the resulting sodium hydroxide is NaOH.

The chief value of the principle of valence in a preliminary course in inorganic chemistry is the assistance it gives in writing formulas. If it were necessary to remember the formula of every compound, the study of chemistry would be tedious and almost hopeless. The application of valence to formula writing can be best illustrated by several examples. Suppose we wish to write the formula of magnesium chloride. From Table A the valence of magnesium is found to be II, and from Table B the valence of chlorine in chlorides is found to be I; therefore, it is necessary to take two atoms of chlorine for one of magnesium in order to balance the valence, and the formula is $\overset{II}{Mg}\overset{I\,I}{Cl_2}$. It is helpful to write the valence as shown in the formula just given, though such a device may be abandoned after the valence of each element and group has been learned. Again, suppose we wish to write the formula of lead nitrate. As in the previous case, from Table A the valence of lead is found to be II, and from Table B the valence of the $NO_3$-group in nitrates is found to be I; therefore it is necessary to take

two $NO_3$-groups to balance the valence of the lead, and the formula is $\overset{II}{Pb}(\overset{II}{NO_3})_2$. Similarly, the formula of sodium sulphate is $\overset{II}{Na_2}\overset{II}{SO_4}$ because two atoms of sodium each having the valence I are needed to balance the valence II of the $SO_4$-group ; and the formula of aluminium hydroxide is $\overset{III}{Al}(\overset{III}{OH})_3$ because three OH-groups each having the valence I are needed to balance the valence of one atom of aluminium having the valence III. Furthermore, suppose we wish to write the formula of a compound formed by the interaction of aluminium and hydrochloric acid. The valence of aluminium is found from Table A to be III, and that of hydrogen to be I. Therefore one atom of aluminium displaces three atoms of hydrogen, and the formula is $\overset{III}{Al}\overset{III}{Cl_3}$. Finally, the formulas of acids, although usually learned by continued observation, can readily be written by utilizing Table B. Acids may be regarded as compounds formed by the union of hydrogen with radicals and elements in Table B. That is, to write the formula of an acid it is only necessary to prefix the proper number of hydrogen atoms to the atom or group in the table, remembering, of course, the rules for naming acids. Thus, the formula of chloric acid is $\overset{I}{H}\overset{I}{ClO_3}$, because the valence of $ClO_3$ is I, and this valence is balanced by one atom of hydrogen; similarly, nitrous acid is $\overset{I}{H}\overset{I}{NO_2}$, phosphoric acid (ortho) is $\overset{III}{H_3}\overset{III}{PO_4}$, silicic acid is $\overset{II}{H_2}\overset{II}{SiO_3}$.

The student is advised to write the formulas of many compounds until valence and its application become thoroughly familiar. (See Exercises at the end of this chapter.)

The valence of elements and atomic groups may be represented in various ways. One has already been given, viz. $\overset{II}{O}$, $\overset{I}{Cl}$, $\overset{II}{SO_4}$. Sometimes short lines are used, *e.g.* H−, O=, or −O−, Al≡, etc. If lines are used to indicate valence in

compounds, a single line answers for two elements. Thus, the formula of water is H – O – H rather than H – – O – – H. Similarly, ammonia gas is $N\begin{matrix}/H\\—H\\\backslash H\end{matrix}$ and calcium hydroxide is $Ca\begin{matrix}/OH\\\backslash OH\end{matrix}$. The length and direction of the lines have no significance provided they indicate the correct valence of the elements in the compound. Such formulas are called **structural** or **graphic formulas**, and they often serve to show what is known about the arrangement of the atoms in a molecule. Structural formulas are especially useful in organic chemistry.

The formulas of certain compounds do not conform to the simplified conception of valence discussed above. Carbon monoxide (CO), calcium carbide ($CaC_2$), lead tetroxide ($Pb_3O_4$), magnetic iron oxide ($Fe_3O_4$), nitric oxide (NO), nitrogen tetroxide ($NO_2$), acetylene ($C_2H_2$), and ethylene ($C_2H_4$) are the common exceptions.

## Problems and Exercises

1. The vapor densities of certain gases (referred to oxygen) are as follows: (*a*) hydrochloric acid 1.14, (*b*) chlorine 2.218, (*c*) ammonia .53125, (*d*) nitrogen .875, (*e*) steam .5625. Calculate the molecular weight of each.

2. Calculate the simplest formula of the compounds which have the indicated composition : (*a*) N = 82.353, H = 17.647; (*b*) O = 30, Fe (iron) = 70; (*c*) H = 1, C = 12, K (potassium) = 39, O = 48.

3. A liter of sulphurous oxide gas ($SO_2$) weighs 2.8672 gm. What is the molecular weight of this compound?

4. If 1500 cc. of carbon monoxide gas (CO) weigh 1.8816 gm., what is the molecular weight of the compound?

5. Calculate the molecular formula of the compounds corresponding to the following data: (*a*) C = 73.8, H = 8.7, N = 17.1, vapor density = 5.03 ; (*b*) C = 92.3, H = 7.7, vapor density = 2.425; (*c*) C = 39.9, H = 6.7, O = 53.4, vapor density = 1.906. (Vapor density in each case is referred to oxygen.)

6. What volumes of factors and products are represented by the equations (*a*) $H_2 + Cl_2 = 2\ HCl$, (*b*) $2\ H_2 + O_2 = 2\ H_2O$, (*c*) $3\ H_2 + N_2 = 2\ NH_3$, (*d*) $N_2 + O_2 = 2\ NO$, (*e*) $2\ NO + O_2 = 2\ NO_2$?

7. If 20 l. of hydrogen are allowed to interact with 10 l. of chlorine, (*a*) how many liters of hydrochloric acid gas are produced, and (*b*) which gas and how much remains?

8. How many liters of hydrogen gas can be obtained from 4 l. of hydrochloric acid gas?

9. If 91.462 gm. of silver, when heated in chlorine, yield 121.4993 gm. of silver chloride, what is the atomic weight of chlorine? (Assume Ag = 108.)

10. How many liters of the component gases can be obtained by the decomposition of 6 l. of ammonia gas?

11. Find the simplest formulas of the substances having the following composition: (*a*) H = 1.58, N = 22.22, O = 76.19; (*b*) O = 47.52, N = 13.86, K = 38.61.

12. A certain weight of copper oxide, when heated in a current of hydrogen, lost 59.789 gm. of oxygen and formed 67.282 gm. of water. (*a*) If O = 16, what is the atomic weight of hydrogen? (*b*) If H = 1, what is the atomic weight of oxygen?

13. One gram of a certain metal was dissolved in hydrochloric acid and gave 1242 cc. of hydrogen at 0° C. and 760 mm. The specific heat was found to be .23. Calculate the equivalent weight and the atomic weight. What would be the valence of the metal? The formula of its chloride?

14. If 2 gm. of carbon unite with 5.33 gm. of oxygen to form a gaseous compound, what is (*a*) the simplest formula, and (*b*) the molecular formula? (At. wt. C = 12 and O = 16; vapor density referred to oxygen = 1.375.)

15. If .1 gm. of a metal gives 34.15 cc. of dry hydrogen at 0° C. and 760 mm., what is the equivalent weight of the metal?

16. Calculate the simplest formulas of the following compounds: (*a*) an oxide containing 70 per cent of iron; (*b*) Zn = 22.7, O = 22.28, S = 11.15, $H_2O$ = 43.87.

17. Suppose 13.67 gm. of a compound of lead and oxygen contained 12.39 gm. of lead and 1.28 gm. of oxygen. What is its formula, if the atomic weight of lead is 206.9?

18. Suppose 45.731 gm. of silver form 60.749 gm. of silver chloride. Calculate the equivalent of silver, if 35.45 is the equivalent of chlorine.

19. Write the formula of the chloride of potassium, sodium, silver, copper (ous), copper (ic), mercury (ous), mercury (ic), iron (ous),

iron (ic), cadmium, zinc, tin (ous), tin (ic), calcium, barium, magnesium, strontium, cobalt, nickel, bismuth, aluminium, carbon, ammonium, antimony (two), phosphorus (two). (Two means -ous and -ic.)

20. Write the formula of the sulphide of K, Na, Ag, Cd, Zn, Ca, Ba, Co, Ni, $NH_4$, As (two), Sb (two), Sn (two), Pb, Fe (ous).

21. Write the formula of the sulphate of K, Na, Ag, Cu, Fe (ous), Cd, Zn, Pb, Ca, Ba, Co, Mg, Ni, Mn, Sr, Cr, Al, $NH_4$.

22. Write the formula of the nitrate of each element mentioned in Problem 21.

23. Write the formula of the hydroxide of $NH_4$, Al, K, Na, Ca, Mg, Ba, Fe (ic), Ni, Co, Cd, Zn, Cr, Bi.

24. Write the formula of the potassium compound of the elements and radicals given in Table B (under Valence, above). Do the same with Ca and Mg.

25. Write the formula of copper acetate, lithium chlorate, manganese dioxide, ammonium fluoride, sodium silicate, potassium manganate, barium phosphate, zinc iodide, ammonium chromate, silver chromate, lead acetate, cobalt nitrite, magnesium oxide, sodium dichromate.

26. Write the formula of aluminium oxide, auric chloride, ferrous bromide, ferrous carbonate, mercurous nitrate, platinum chloride, aluminium phosphate, calcium fluoride, potassium cyanide, hydrocyanic acid, sodium permanganate.

27. Write the formula of phosphoric acid silicic acid, sulphurous acid, nitrous acid, chromic acid, acetic acid, hydriodic acid.

28. By the Victor Meyer method .1561 gm. of a compound expelled 32.1 cc. of dry air at 20° C. and 744 mm. Calculate its vapor density and its molecular weight.

Review

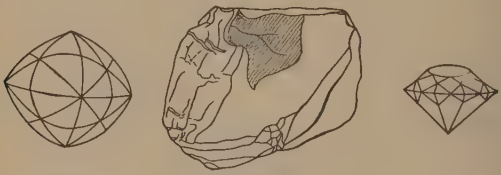
# CHAPTER XV

## Carbon and its Oxides — Carbides

**Occurrence of Carbon.** — Uncombined carbon is found pure in nature as diamond and graphite ; in a more or less impure state it occurs as coal and similar substances, which are included in the term *amorphous carbon.* Combined with hydrogen and oxygen, and occasionally with nitrogen also, it is an essential constituent of animal and vegetable matter. Meat, starch, fat, sugar, wood, cotton, wool, wax, flour, albumen, and bone are familiar examples of the vast number of natural substances which contain carbon. It is also a constituent of carbon dioxide and of the carbonates, such as limestone, chalk, marble, and dolomite. Illuminating gases, gasolene, kerosene (and other products obtained from petroleum), turpentine, alcohol, chloroform, ether, and similar liquids are compounds of carbon. Carbon is also a constituent of thousands of artificial substances, such as dyestuffs, medicines, and perfumes.

**Diamond** is pure crystallized carbon. It is found in only a few places in the earth. When taken from the mine, diamonds are usually rough-looking stones ; some are crystals, some are rounded like peas, and many are irregular ; they must be cut into special shapes and polished to bring out the luster and make them sparkle (Fig. 28). The highly prized diamonds are colorless and without a flaw and are said to be "of first water"; yellow ones from South Africa are common, and occasionally a blue, pink, or green one is found ; a very impure variety is black.

The diamond is insoluble in all liquids at the ordinary temperature, has the high specific gravity of 3.5, and is the hardest known substance. It is brittle, and may be shattered by a blow with a hammer.



Crystal Rough Cut

FIG. 28. — Diamonds.

Diamonds have always been prized as gems on account of their beauty, rarity, and permanence. Besides being worn as jewels, they are used to cut glass, and the powder and splinters (known as **bort**) are used to grind and polish diamonds and other hard gems. The impure variety is called **carbonado**, and is set into the end of the "diamond drill," which is used extensively for boring artesian wells and drilling hard rocks.

The diamond was formerly found in gravel deposits in India, and in later years in Brazil. Since 1867, however, about 95 per cent of the diamonds of commerce have come from South Africa. They occur in a bluish volcanic rock along the Vaal River, and especially near Kimberley. Nearly ten tons of diamonds have been found in South Africa in the last twenty-five years!

The successive investigations of Lavoisier, Dumas, and Davy, extending from 1772 to 1814, showed that diamond is carbon, for when pure diamond was burned in oxygen, the only product was carbon dioxide. This result, which admits of no doubt, has been verified by many famous investigators. Diamonds have been made by Moissan. He dissolved pure charcoal in melted iron, and cooled the molten mass in water. The surface was so suddenly cooled that a tremendous pressure was exerted by the expanding iron inside the crust. This pressure caused the

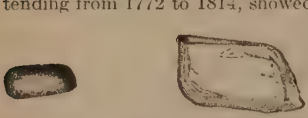


FIG. 29. — Artificial diamonds (enlarged) prepared by Moissan.

cooling carbon to crystallize into diamond. The crystals were very small, most of them black, a few were white, but all had the properties of the diamond (Fig. 29).

Large diamonds have a fascinating history, since most of them passed through many hands before becoming royal jewels. Until recently the largest royal cut diamond was the Orloff, which weighs 194¾ carats, and is in the scepter of the Czar of Russia.[1] The Kohinoor, which now weighs about 106 carats, is one of the crown jewels of England. The largest diamond thus far known is the Cullinan. It was found in South Africa in 1905, and was presented to the king of England in 1907. It weighed (uncut) 3024¾ carats (1.37 lb. avoir.).

**Graphite** is a soft, black, shiny solid, which is smooth and greasy to the touch. Pure graphite is entirely carbon. It occurs native in large quantities and in many places. One variety is found in abundance at Ticonderoga, New York. Other famous localities are Ceylon, Siberia, Germany, Austria, and Italy. Sometimes crystals and grains are found, but it usually occurs in flaky masses or slabs. Unlike diamond, graphite is a good conductor of electricity and is often used to coat molds in electrotyping. It is so soft that it blackens the fingers and leaves a black mark on paper when drawn across it. This property is indicated by the name *graphite*, which is derived from a Greek word (*graphein*) meaning to write. It resembles diamond in its insolubility in liquids at the ordinary temperature. Its specific gravity is about 2.2, being considerably lighter than diamond. When heated intensely in a current of oxygen, it is converted into carbon dioxide ; but it can be heated to a very high temperature in the air without undergoing chemical change. Graphite was once supposed to contain lead, and is even now often incorrectly called "black lead" and plumbago. It is used to make stove polish and protective paints, as a lubricant where oil would be decomposed by the heat, as the principal ingredient of the

[1] The international carat weighs .205 gm. (equals 3.174 Troy grains).

graphite crucibles which withstand extremely high temperatures, and in making electrodes for electric furnaces and electrolytic apparatus. Large quantities of graphite are consumed in the manufacture of lead pencils. The graphite is washed free from impurities, ground to a fine powder, mixed with more or less clay, according to the hardness desired, and then passed through perforated plates, from which the "lead" issues in tiny rods. These are dried, cut into proper lengths, baked to remove all traces of moisture, and then inserted in the wooden case.

Molten iron and other metals dissolve carbon, and when the metals cool, the carbon crystallizes as graphite. Moissan incidentally obtained considerable graphite in making diamonds. Artificial graphite is now manufactured on a large scale by heating a special grade of coal or of coke in an electric furnace. The process is electrothermal, and yields a product that is exceptionally suitable for electrodes.

**Amorphous Carbon** is a broad term, including all varieties of coal and charcoal, lampblack, and gas carbon. They are the non-crystalline varieties of impure carbon, and differ mainly in purity, degree of fineness, and hardness. The word *amorphous* means literally "without form," and is often used to designate soft, powdery substances, but more especially those which are uncrystallized.

**Coal** is the term applied to several varieties of impure carbon. It may be regarded as the final product derived from vegetable matter which was subjected to heat and pressure through long geological periods. Ages ago the vegetation was exceedingly dense and luxuriant upon land slightly raised above the sea. In the process of time this vegetation decayed, accumulated, and slowly became covered with sand, mud, and water. Owing to the heat of the earth and the enormous pressure of the overlying deposits, the

complex vegetable matter decomposed slowly into carbon and compounds of hydrogen and carbon called hydrocar-

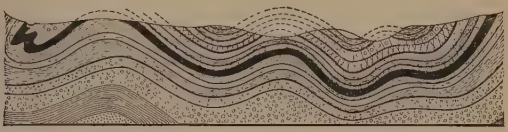


FIG. 30. — Section of part of the earth's crust near Mauch Chunk, Pennsylvania, showing layers of coal.

bons. The geological and chemical changes were repeated, and as a result we find in the earth layers or seams of carbonaceous matter varying in thickness and composition (Fig. 30). These are the coal beds. Coal beds contain proofs of their vegetable origin, viz. impressions of vines, stems, leaves of plants, and similar vegetable substances (Fig. 31).

FIG. 31. — Fossil found in a coal bed.

FIG. 32. — Section of coal as seen through a microscope.

A thin section of coal examined through a microscope reveals a distinct cellular structure characteristic of vegetable matter (Fig. 32). The transformation of vegetable matter into coal was an exceedingly slow process, espe-

cially where the rocks were undisturbed. In some localities the process was hastened by deep-seated changes incidental to the upheaval of the rocks during mountain building; the gaseous products escaped almost completely and left the carbon, together with a small proportion of mineral matter. Consequently we find several varieties of coal in the earth's crust. There are three main classes — anthracite, bituminous, and lignite, though commercially several subclasses are variously designated. They

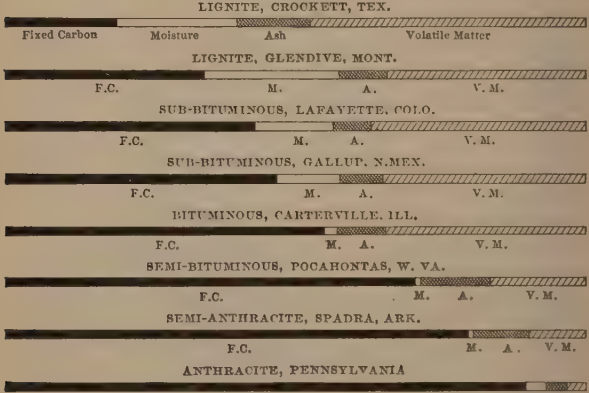



FIG. 33. — Diagram showing the progressive change in composition of coal. (From *National Geographic Magazine.*)

differ in composition. That is, they contain different proportions of moisture, ash or mineral matter, volatile matter or compounds of carbon and hydrogen driven off by careful heating, and fixed carbon or carbon left after the removal of the volatile matter and ash. The progressive change in composition from a very poor lignite to the best anthracite is shown in Figure 33. The diagram also shows the com-

position as determined by proximate analysis, *i.e.* a chemical analysis designed to find the per cent of the components mentioned above and not the actual per cent of carbon, hydrogen, etc. From the diagram it is seen that the fixed carbon (F.C.) varies from about 20 per cent in the lignite to about 90 per cent in the anthracite, while the volatile matter (V.M.) varies inversely as the fixed carbon, being greatest in the lignite and least in the anthracite. The per cent of moisture (M.) diminishes from the lignite to the anthracite. The per cent of ash (A.) is variable.

The properties and uses of coal differ with the composition. **Anthracite coal** is hard and lustrous. It ignites with difficulty, burns with a slight or no flame, and produces an intense heat. It is used mainly for domestic purposes, — heating and cooking, — especially in the eastern United States. **Bituminous** or **soft coal** burns with a smoky flame, and in burning produces considerable volatile matter; some varieties form coke when heated. It is used to make illuminating gas, coke, and as a fuel for generating steam. **Lignite** or **brown coal** is the least valuable as fuel. The use of coal as fuel depends, of course, on the fact that considerable heat is liberated when it burns; that is, it has calorific value. The following table shows the calorific value of well-known commercial grades of the three classes of coal in calories per gram, *i.e.* the number of calories liberated when 1 gm. is burned freely: —

Calorific Value of Coal

| Class | Calories per Gram |
|---|---|
| Anthracite | 7724 |
| Bituminous | 8768 |
| Lignite | 4530 |

Coal is widely distributed in the crust of the earth, but the deposits vary in extent and quality. It underlies about one sixth of the area of the United States, the anthracite variety covering less than five hundred square miles in eastern Pennsylvania (Fig. 34). The United

FIG. 34. — Map showing coal areas in the United States. The black areas are anthracite and bituminous; the shaded areas are lignite. (From *National Geographic Magazine.*)

States now leads the world in coal production, furnishing about one third of the total supply. England for many years headed the list, and even now furnishes a large amount, for its deposits are extensive.

**Charcoal** is a variety of amorphous carbon obtained by heating wood, bones, ivory, and other organic matter in closed vessels, or by partially burning them in the air. There are several varieties. **Wood charcoal** is a black, brittle solid, and often has the shape of the wood from which it is made. It is insoluble, though its mineral impurities can be removed by acids. It burns without a flame or much smoke, and leaves a white ash. The compact

varieties conduct heat and electricity, but porous charcoal is a poor conductor. It resists the action of moisture and many chemicals; hence fence posts, telegraph poles, and wooden piles are often charred before being put into the ground. Most varieties are very porous, and when thrown upon water a lump of charcoal floats for some time, owing to the presence of air in its pores. Its porosity makes charcoal an excellent absorber of gases, some varieties absorbing ninety times their bulk of ammonia gas. Sewers and foul places are sometimes temporarily purified by charcoal. It also absorbs colored substances from solutions. This is especially true of animal charcoal. (See below.) Foul air and water may be partially purified by charcoal, which forms the essential part of many filters in houses. Charcoal used for such a purpose, however, must be frequently renewed or often heated to redness; otherwise it becomes clogged or contaminated. Charcoal is never pure carbon, the degree of purity depending upon the kind of wood used, as well as the temperature and method employed.

Besides the uses of charcoal mentioned above, it is used as a fuel, in the manufacture of steel and of gunpowder, and as a medicine. It reduces oxides when heated with them, thus: —

$$\underset{\text{Copper Oxide}}{2\,CuO} + \underset{\text{Carbon}}{C} = \underset{\text{Copper}}{2\,Cu} + \underset{\text{Carbon Dioxide}}{CO_2}$$

Wood charcoal is made either in a charcoal pit or kiln, or in a large retort. Where wood is plentiful, it is loosely piled into the shape shown in Figure 35, and covered with turf to prevent too free access of air, though small holes are left at the bottom and a larger one at the top (as a central flue), so that sufficient air can pass through the pile. The wood is lighted, and as it slowly burns care is taken to regulate the supply of air, so that the wood will smolder but not be consumed. The volatile matter escapes and the charcoal remains, the average yield being about 20 per cent of the weight of the wood.

This method is crude, uncertain, and wasteful. Much charcoal is now made by heating wood in closed retorts, no air whatever being admitted. By this method, which is called dry or destructive distillation, the yield of charcoal is 30 per cent, and all the volatile matter

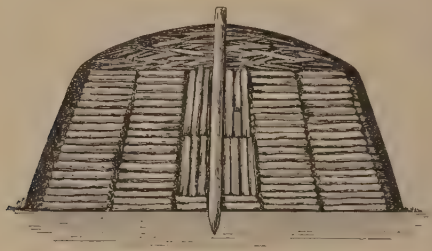


FIG. 35. — Wood arranged for burning into charcoal.

is saved. In the ordinary combustion of wood, the hydrogen forms water and the oxygen forms carbon dioxide; but in dry distillation, where no oxygen is present, much of the hydrogen forms volatile compounds with the carbon and oxygen. Among these volatile products are methyl alcohol ($CH_4O$), acetone ($C_3H_6O$), and acetic acid ($C_2H_4O_2$). These are commercial substances, and contribute to the profit of the process. More or less charcoal is obtained by heating any compound of carbon, *e.g.* sugar or starch, the charring being a **test for carbon.** Such charcoal, especially that obtained from sugar, is very pure.

**Animal Charcoal** or **Bone Black** is made by heating bones in a closed vessel, or by heating a mixture of blood and sodium carbonate. It contains only about 10 per cent of carbon, but this carbon is distributed throughout the porous mineral matter of the bone. Under the name of ivory black, animal charcoal is used as a pigment, especially in making shoe-blacking. Bone black is extensively used to decolorize sugar sirups, oils, and other liquids colored by organic matter.

**Coke** is made by expelling the volatile matter from bituminous coal, somewhat as charcoal is made from wood. It is left in the retorts when coal is distilled in the manufacture of illuminating gas. On a large scale it is made by heating a special grade of bituminous coal in huge ovens, often shaped like a beehive, from which air is excluded soon after combustion begins. Sometimes the coke is made in closed retorts constructed to save the by-products, — tar, ammonia (in the form of ammonium sulphate or ammoniacal liquor), organic compounds (such as benzene, phenol, and pyridine), and combustible gases. This method not only yields more coke, but is also more profitable because the by-products are sold and the combustible gas is used as a source of heat, light, and power. Coke is a grayish, porous, coherent solid, harder and heavier than charcoal. It burns with no smoke and a feeble flame. It contains about 90 per cent of carbon, the rest being the mineral matter originally in the coal. Immense quantities of coke are used in the manufacture of iron and steel. It is superior to coal for this purpose, because it gives a greater heat when burned, reduces oxides easily, and contains little or no sulphur or other substances which would impair the metallic product. The calorific value of Connellsville coke is about 7900 calories per gram. Coke is the fuel used in making nine tenths of the pig iron in the United States, and over twelve million tons (or about three fourths of the total amount) are made annually in the Connellsville district, near Pittsburg, Pennsylvania.

**Gas Carbon** is the variety of amorphous carbon which is gradually deposited upon the inside of the retorts during the manufacture of illuminating gas. It is a black, heavy, hard solid, and is almost pure carbon. It is a good conductor of electricity, and is utilized to some extent for the

manufacture of the carbon electrodes used in electric lights and electric batteries.

**Lampblack** is prepared by burning certain oils and resinous substances rich in carbon in a limited supply of air. The dense smoke, which is mainly finely divided carbon, is passed through a series of condensing chambers, where it is collected upon coarse cloth or a cold surface. Its formation is illustrated on a small scale by a smoking lamp, the deposited soot being substantially the same as lampblack. Lampblack is one of the purest forms of amorphous carbon, and is used in making printer's ink and certain black paints.

**Allotropism.** — Diamond, graphite, and pure amorphous carbon (*e.g.* sugar charcoal), though exhibiting essentially different properties, are identical in composition. All are carbon. They can be changed into one another without leaving a residue, the amorphous form into graphite and finally into diamond, and the diamond itself into amorphous carbon. Each burns in oxygen, and the sole product is carbon dioxide. Furthermore, a given weight of each yields the same weight of carbon dioxide, *e.g.* when 12 gm. of each are burned, 44 gm. of carbon dioxide are always produced. There is no doubt about their identity. Elements which exist in two or more distinct varieties are called allotropic, and the property of assuming more than one variety is called **allotropism** or **allotropy** (from Greek words meaning "another form"). One variety is called an **allotrope** or an allotropic modification of the other. Allotropism is believed by many to be due to a difference in the number of atoms in a molecule of the element, and by others to a difference in the amount of energy in the substance.

**Chemical Properties of Carbon.** — Carbon unites directly with many elements, though the temperature must usually

be raised to bring about combination. Fluorine is the only element with which it unites at ordinary temperatures. The formation of acetylene ($C_2H_2$) from carbon and hydrogen takes place at the temperature of the electric arc. Carbon unites with many metals and non-metals at the high temperatures produced in the electric furnace, thereby forming **carbides**. (See end of this chapter.) It also unites directly with sulphur to form carbon disulphide ($CS_2$) in a special form of furnace. A conspicuous and important chemical property of carbon is its behavior with oxygen. It unites directly with oxygen at elevated temperatures to form carbon dioxide ($CO_2$) or carbon monoxide (CO), depending upon conditions which are discussed under these gases. Considerable heat is developed during the uniting with oxygen. The use of various forms of carbon and carbonaceous substances as fuel is based on this fact. The thermal equation for the transformation of carbon (in the form of charcoal) into carbon dioxide is —

$$\underset{\text{Carbon}}{C} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + 97{,}000 \text{ cal.}$$

Carbon reduces oxides, a simple illustration being the reduction of copper oxide, thus: —

$$\underset{\substack{\text{Copper}\\\text{Oxide}}}{2\,CuO} + \underset{\text{Carbon}}{C} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\text{Copper}}{2\,Cu}$$

This property is applied in the reduction of ores of iron and other metals.

### Oxides of Carbon

Carbon and oxygen do not unite at the ordinary temperature. But when carbon is heated in air, in oxygen, or with some oxides, carbon dioxide ($CO_2$) is usually formed;

if the supply of oxygen is limited, carbon monoxide (CO) is also formed.

**Occurrence and Formation of Carbon Dioxide.** — The occurrence of carbon dioxide in the atmosphere (3 to 4 parts in 10,000) and in many natural waters (especially mineral waters) has already been mentioned. It is one product of ordinary combustion, respiration of animals, fermentation, and decay; in all these processes the carbon comes from organic matter, while the oxygen comes for the most part from the air, though some is supplied by the organic matter.

Ordinary combustion is the chemical combining of carbon and oxygen. Hence, when carbon or a substance containing it is burned in an excess of air or oxygen, carbon dioxide is formed. The equation for this chemical change is —

$$\underset{\text{Carbon}}{C} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2}$$

Carbon dioxide is formed, therefore, by the combustion of such common carbonaceous substances as wood, coal, charcoal, coke, oils, waxes, cotton, bone, starch, sugar, meat, bread, alcohol, camphor, and illuminating gas.

The continuous oxidation of the tissues of the body produces carbon dioxide. (See Relation of Oxygen to Life.) And if we exhale the breath through a glass tube into calcium hydroxide (limewater), the carbon dioxide which is in the breath turns the limewater cloudy or turbid — the usual **test for carbon dioxide**. The equation for the change is —

$$\underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{Carbonate}}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

When vegetable and animal matter decays, carbon dioxide is one product. Many kinds of organic matter ferment,

especially those containing certain kinds of sugar. By alcoholic fermentation the sugar changes into carbon dioxide and alcohol (see Alcohol), thus: —

$$\underset{\text{Sugar}}{C_6H_{12}O_6} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{2\,CO_2} + \underset{\text{Alcohol}}{2\,C_2H_6O}$$

**The Preparation of Carbon Dioxide** is accomplished in the laboratory by the interaction of a carbonate and an acid. Calcium carbonate (limestone or marble) and dilute hydrochloric acid are usually used. The equation for the chemical change is —

$$\underset{\substack{\text{Calcium}\\\text{Carbonate}}}{CaCO_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid}}}{2\,HCl} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\substack{\text{Calcium}\\\text{Chloride}}}{CaCl_2} + \underset{\text{Water}}{H_2O}$$

This gas may also be prepared by burning matter containing carbon and by strongly heating carbonates (as in making lime), thus: —

$$\underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6\,O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{6\,CO_2} + \underset{\text{Water}}{6\,H_2O}$$

$$\underset{\substack{\text{Calcium}\\\text{Carbonate}}}{CaCO_3} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\text{Lime}}{CaO}$$

**Properties of Carbon Dioxide.** — This gas has many important properties besides those mentioned under The Atmosphere. It has a slight taste and odor, but no color. It is one and a half times heavier than air, and a liter under standard conditions weighs 1.977 gm. On account of its weight it is usually collected by the displacement of air (like chlorine and hydrochloric acid gas). Its weight is also one reason why it collects at the bottom of abandoned or deep wells, in some valleys near volcanoes, and in mines after explosions. At the ordinary temperature and pressure, water dissolves its own volume of carbon dioxide. Under

increased pressure more gas dissolves, which escapes to some extent when the pressure is removed. (See Carbonic Acid, below.) Hence "soda water," which is made by forcing carbon dioxide into water, effervesces and froths when drawn from the soda fountain. Many natural waters and manufactured beverages (such as champagne) sparkle and effervesce for the same reason. The critical temperature is 31° C. and the critical pressure is about 72 atmospheres. Hence this gas can be readily liquefied. It was first liquefied by Faraday by the method similar to that used for chlorine. **Liquid carbon dioxide** is now made in large quantities by forcing the gas into steel cylinders (by powerful pumps) which are cooled by water during the operation; the gas is sometimes obtained from the fermenting vats of breweries, though often prepared by decomposing magnesium or calcium carbonate. When liquid carbon dioxide is allowed to escape into the air, a portion evaporates quickly and thereby withdraws heat from the remainder; if sufficiently cooled, it becomes white, snowlike, solid carbon dioxide. The latter is used to produce low temperatures; a paste of ether and solid carbon dioxide has a temperature of — 80° C., and in a vacuum it may fall to — 100° C.

Carbon dioxide does not burn, but extinguishes many burning substances, such as a blazing stick or lighted candle, the latter being used occasionally to detect carbon dioxide in wells, caves, and mines. Air containing from 2.5 to 4 per cent of carbon dioxide will extinguish small flames. Hence the gas is sometimes used to extinguish fires. A stream of gas forced upon a small blaze will often prevent a serious fire. In the portable fire extinguishers and chemical engines, the carbon dioxide is generated rapidly by the interaction of sulphuric acid and sodium bicarbonate ($HNaCO_3$), and the generated gas forces the water from the extinguisher upon the fire.

Carbon dioxide is reduced by heated carbon into carbon monoxide, thus: —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon Monoxide}}{2\,CO}$$

Several metals also decompose carbon dioxide. With moderately heated zinc the chemical change is expressed thus: —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc Oxide}}{ZnO} + \underset{\text{Carbon Monoxide}}{CO}$$

With burning magnesium, sodium, or potassium the chemical change is as follows: —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Magnesium}}{2\,Mg} = \underset{\text{Magnesium Oxide}}{2\,MgO} + \underset{\text{Carbon}}{C}$$

Carbon dioxide combines directly with several oxides, thus: —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Calcium Oxide}}{CaO} = \underset{\text{Calcium Carbonate}}{CaCO_3}$$

It also unites with water to form carbonic acid ($H_2CO_3$) (see below).

**Relation of Carbon Dioxide to Life.** — Animals die when put into carbon dioxide. It cuts off the supply of oxygen just as water does from a drowning man. The presence of a small quantity in the air is objectionable. On the other hand, carbon dioxide is an essential food of plants. Through their leaves and other green parts they absorb carbon dioxide from the atmosphere, decompose it, reject part of the oxygen, and store up the carbon in the form of starch. The sunlight and the green coloring matter aid the plant in manufacturing its food out of the water (obtained through the roots from the soil) and the carbon of the carbon dioxide obtained from air. Plants in this way help keep the atmosphere free from an excess of carbon dioxide.

**Carbonic Acid.** — Carbon dioxide gas is often called carbonic acid gas, or simply carbonic acid. The latter term when applied to carbon dioxide ($CO_2$) is incorrect. When carbon dioxide is passed into water, it combines to a slight extent with the water and forms a weak, unstable acid, which is, strictly speaking, **carbonic acid.** The equation for this change is —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Carbonic Acid}}{H_2CO_3}$$

Such a solution reddens blue litmus and decolorizes pink phenolphthalein, though its action on these indicators is rather feeble. In terms of the theory of electrolytic dissociation it is a weak acid, *i.e.* it ionizes only to a small degree, the ions being $H^+$ and $HCO_3^-$. Carbonic acid has never been obtained free; it is so unstable that it easily breaks up by gentle heat into carbon dioxide and water, thus: —

$$H_2CO_3 = CO_2 + H_2O$$

Carbon dioxide is sometimes called carbonic anhydride, to denote its relation to the acid. Carbonic acid is dibasic and forms two classes of salts — normal and acid carbonates.

**Carbonates** are salts corresponding to carbonic acid. They are important compounds. The most abundant natural carbonates are those of calcium, magnesium, and iron. Immense quantities of sodium and potassium carbonates are manufactured.

A few carbonates are formed by direct combination of an oxide and carbon dioxide, but many are formed by the interaction of carbon dioxide and a base, thus: —

$$CO_2 + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{Carbonate}}}{CaCO_3} + H_2O$$

Others are formed by the interaction of a soluble carbonate and another soluble salt, and are readily produced, since all except those of sodium, potassium, and ammonium, and certain acid carbonates are practically insoluble in water. There are two classes of carbonates, the **normal** and the **acid**. Normal sodium carbonate is $Na_2CO_3$, and acid sodium carbonate is $HNaCO_3$. The latter is called **sodium bicarbonate**. Normal calcium carbonate is $CaCO_3$, and calcium bicarbonate or acid calcium carbonate is $H_2Ca(CO_3)_2$; the latter salt is unstable, and is decomposed by gentle heat into normal calcium carbonate. The acid calcium carbonate is formed from the normal carbonate by an excess of carbon dioxide. When carbon dioxide is passed into water containing the insoluble normal calcium carbonate in suspension, the soluble acid calcium carbonate is formed, thus: —

$$\underset{\text{Carbonic Acid}}{H_2CO_3} + \underset{\text{Calcium Carbonate}}{CaCO_3} = \underset{\text{Acid Calcium Carbonate}}{H_2Ca(CO_3)_2}$$

Now when this solution of acid calcium carbonate is heated, the decomposition takes place thus: —

$$\underset{\text{Acid Calcium Carbonate}}{H_2Ca(CO_3)_2} = \underset{\text{Calcium Carbonate}}{CaCO_3} + \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Water}}{H_2O}$$

Since many underground waters contain carbon dioxide, these waters dissolve the limestone ($CaCO_3$) over which they pass, forming "hard" water. When the dissolved acid calcium carbonate is decomposed by heat or in some other way, the calcium carbonate is reprecipitated. (See Stalactites (under Calcium Carbonate), Natural Waters, and Hardness of Water.)

**Composition of Carbon Dioxide.** — If a known weight of pure carbon, such as diamond or graphite, is burned in oxygen, it is found that for 12 parts of carbon used there are 44 parts of carbon dioxide formed. Hence 12 parts of carbon unite with 32 parts of oxygen.

Since the vapor density of the gas is 1.375 (if $O_2 = 32$), the molecular weight must be 44. These facts necessitate the formula $CO_2$.

**History of Carbon Dioxide.** — This gas was described in the seventeenth century by Van Helmont, who called it *gas sylvestre*. He prepared it by the interaction of acids and carbonates, detected it in mineral water, and observed its formation during combustion and fermentation, as well as its action on animals and flames. Black, in 1755, showed that carbon dioxide is essentially different from ordinary air, and that the gas is readily obtained from magnesium and calcium carbonates. Since the gas was combined or "fixed" in these substances, he called the gas fixed air. His work was verified in 1774 by Bergman, who called the gas acid of air. Lavoisier first proved it to be an oxide of carbon.

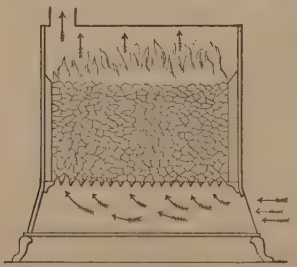
**Carbon Monoxide** is formed when carbon is burned in a limited supply of air, thus: —

$$\underset{\text{Carbon}}{2\,C} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Carbon Monoxide}}{2\,CO}$$

If carbon dioxide is passed over heated charcoal, the product is carbon monoxide. That is, carbon reduces carbon dioxide to carbon monoxide, the equation for the change being —

$$\underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon Monoxide}}{2\,CO}$$

These chemical changes take place in every coal fire (Fig. 36). The oxygen (of the air) entering at the bottom of the



$$2\,CO + O_2 = 2\,CO_2$$

$$CO_2 + C = 2\,CO$$

$$2\,C + 2\,O_2 = 2\,CO_2$$

FIG. 36. — Essential chemical changes during combustion in a coal fire.

fire unites with the carbon to form carbon dioxide; the latter gas in passing through the hot carbon of the fire is reduced to carbon monoxide. Some of the carbon monoxide escapes, while some burns with a flickering bluish flame on the top of the fire, and forms carbon dioxide.

If steam is passed over red-hot coke or charcoal, a mixture of carbon monoxide and hydrogen is produced, thus: —

$$\underset{\text{Water}}{H_2O} + \underset{\text{Carbon}}{C} = \underset{\text{Hydrogen}}{H_2} + \underset{\substack{\text{Carbon}\\\text{Monoxide}}}{CO}$$

This mixture enriched by vapor from oils is known as water gas. (See Water Gas.)

**Preparation of Carbon Monoxide.** — This gas is usually prepared in the laboratory by gently heating a mixture of oxalic acid and sulphuric acid, and collecting the gaseous product over water. The oxalic acid decomposes thus: —

$$\underset{\substack{\text{Oxalic}\\\text{Acid}}}{C_2H_2O_4} = \underset{\substack{\text{Carbon}\\\text{Monoxide}}}{CO} + \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\text{Water}}{H_2O}$$

The carbon dioxide can be removed by passing the mixed gases through a solution of sodium hydroxide.

**Properties of Carbon Monoxide.** — It is a gas without color, odor, or taste, and is only slightly soluble in water. It burns with a bluish flame, forming carbon dioxide, thus: —

$$\underset{\substack{\text{Carbon}\\\text{Monoxide}}}{2\,CO} + O_2 = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{2\,CO_2}$$

Carbon monoxide is extremely poisonous, and it is doubly dangerous because the lack of odor prevents its detection in time to escape its stupefying effect. Many deaths have been caused by breathing air containing it. Carbon monoxide forms a rather stable compound with the hæmoglobin of the blood, and persons who have been poisoned by it

cannot usually be revived by air, as in the case of suffocation by carbon dioxide. It is an ingredient of water gas and most ordinary illuminating gas. Care should always be taken to prevent the escape of illuminating gas (as well as the gas from a coal stove or furnace) into occupied rooms. At a high temperature carbon monoxide readily removes combined oxygen, and is, therefore, an important reducing agent, *e.g.* in the manufacture of iron from iron ores in the blast furnace. This chemical change may be represented thus :—

| $Fe_2O_3$ | + | $3\,CO$ | = | $2\,Fe$ | + | $3\,CO_2$ |
|---|---|---|---|---|---|---|
| Iron Oxide | | Carbon Monoxide | | Iron | | Carbon Dioxide |

Carbon monoxide, which is sometimes called carbonic oxide, forms no acid, and therefore no salts. It does not turn calcium hydroxide (limewater) milky, thus being readily distinguished from carbon dioxide. Its blue flame distinguishes it from all other gases which burn. It unites directly with chlorine, to form carbonyl chloride (phosgene, $COCl_2$), and with some metals, forming metallic carbonyls, *e.g.* nickel carbonyl ($Ni(CO)_4$).

### Carbides

**Carbides** are compounds of carbon and certain elements, especially metals. They are numerous, owing to their ready formation when carbon and oxides are heated in an electric furnace. Calcium carbide and silicon carbide are important commercial substances. Several carbides yield compounds of carbon and hydrogen by interaction with water, acetylene ($C_2H_2$) and methane ($CH_4$) being commonly formed.

**Calcium carbide**, $CaC_2$, is made on a large scale by heating a mixture of lime and coke (a form of carbon) in an electric

furnace. The chemical change is caused solely by the intense heat, and may be represented thus: —

$$\underset{\text{Carbon}}{3\,C} + \underset{\text{Lime}}{CaO} = \underset{\substack{\text{Calcium}\\\text{Carbide}}}{CaC_2} + \underset{\substack{\text{Carbon}\\\text{Monoxide}}}{CO}$$

This method of making calcium carbide cheaply was discovered independently and at about the same time (1892–1895) by Moissan and Willson. The electric furnaces now in use are of the resistance type, and although differing in details, all have one essential feature, viz. the generation of heat by the passage of an electric current through a charge of materials offering a high resistance.

Calcium carbide is a hard, brittle, dark gray, crystalline solid. Its specific gravity is about 2.2. The most striking and useful property is its action with water, acetylene being formed, thus: —

$$\underset{\substack{\text{Calcium}\\\text{Carbide}}}{CaC_2} + \underset{\text{Water}}{2\,H_2O} = \underset{\text{Acetylene}}{C_2H_2} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{Ca(OH)_2}$$

Calcium carbide is used to generate acetylene gas. This gas burns with a brilliant flame, and is coming into general use as an illuminant. Owing to its vigorous action with water, calcium carbide is packed and sold in air-tight cans. (See Acetylene.)

**Silicon carbide**, SiC, is a very hard, dark-colored crystalline solid prepared by heating coke and sand (silicon dioxide) in an electric furnace. (See Carborundum.)

### Problems and Exercises

1. The specific gravity of charcoal is about 1.5. Why does it float on water?

2. How many grams of calcium carbonate are needed to prepare 132 gm. of carbon dioxide?

3. What weight of carbon burned in air will produce 11 gm. of carbon dioxide?

4. Calculate the percentage composition of (*a*) calcium carbonate, (*b*) magnesium carbonate.

5. What per cent of carbon (by weight) is contained in carbon monoxide and in carbon dioxide?

6. If 20 gm. of carbon are heated in the presence of 44 gm. of carbon dioxide, (*a*) what weight of carbon monoxide is formed, and (*b*) what weight, if any, of carbon remains?

7. How many liters of carbon dioxide must be passed over red-hot charcoal to yield 84 gm. of carbon monoxide?

8. How much carbon dioxide (*a*) by weight, and (*b*) by volume, is in the air of a room 6 m. long, 4 m. wide, and 3 m. high, if there is 1 vol. of carbon dioxide in 1000 vol. of air?

9. What weight of water must be decomposed to furnish enough oxygen to form (with pure carbon) 44 gm. of carbon dioxide?

10. How many grams of calcium carbonate will produce 15 l. of carbon dioxide?

11. If a piece of pure graphite weighing 7 gm. is burned in oxygen, what volume of carbon dioxide is formed?

12. The Cullinan diamond weighed 3024¾ carats. Calculate its weight in pounds (avoir.), grams, and grains (Troy).

13. How many cubic centimeters of hydrochloric acid containing 36 per cent of hydrogen chloride (HCl) are needed to decompose 26 gm. of pure calcium carbonate? How much $CO_2$ by weight and by volume (at 0° and 760 mm.) would be liberated?

14. Calculate the per cent of carbon in calcium carbide ($CaC_2$).

15. An oxide of carbon contains 42.85 per cent of carbon. Calculate its simplest formula. Calculate the molecular formula if a liter of the gas weighs 1.25 gm. under standard conditions.

16. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): barium carbonate, ammonium carbonate, ferrous carbonate, acid calcium carbonate, acid potassium carbonate, acid sodium carbonate.

17. Interpret the following equations:—

$$\underset{\text{Diamond}}{C} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + 93{,}250 \text{ cal.}$$

$$\underset{\substack{\text{Gas}\\\text{Carbon}}}{C} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + 96{,}500 \text{ cal.}$$

18. Carbon and oxygen combine in the ratios (*a*) 3 : 4 and (*b*) 3 : 8. Write the simplest equation expressing each of these ratios.

19. Write equations corresponding to the following reactions: (*a*) Lead oxide (PbO) and carbon form lead and carbon dioxide. (*b*) Carbon dioxide and barium hydroxide form barium carbonate and water. (*c*) Magnesium carbonate and hydrochloric acid form carbon dioxide, magnesium chloride, and water.

20. Calculate the percentage composition of carbon dioxide and carbon monoxide, and restate the percentages in a form which illustrates the law of multiple proportions.

21. Change the following ordinary chemical equations into molecular equations, and write the correct gas volumes under the gaseous substances : —

(*a*) $CO + O = CO_2$

(*b*) $C + O = CO$

22. State how the final equations in Problem 21 illustrate Gay-Lussac's law.

## CHAPTER XVI

**Hydrocarbons — Methane — Ethylene — Acetylene — Illuminating Gas — Flame — Bunsen Burner — Oxidizing and Reducing Flames**

HYDROCARBONS are compounds of carbon and hydrogen. They number about two hundred and fifty. Their properties as individuals vary between wide limits, but as a class the hydrocarbons are rather indifferent in chemical behavior. They are found in petroleum and its products (kerosene, naphtha, lubricating oils, paraffin wax, etc.), in coal tar, in coal gas and natural gas, and in some essential oils, such as turpentine. On a large scale they are prepared by the distillation of petroleum, wood, coal, and coal tar. Indirectly the hydrocarbons are the source of many other compounds of carbon, which are extensively used in numerous industries; several of these organic compounds, as they are called, will be described in the next chapter.

**Methane**, $CH_4$, is the simplest hydrocarbon. It is found in coal mines, being a gaseous product of the processes which changed vegetable matter into coal. It is called fire damp by miners. It is also formed in marshy places by the decay of vegetable matter under water, and is therefore often called marsh gas. It is the main constituent of natural gas, and forms a large proportion of the illuminating gas obtained by heating coal.

Methane is usually prepared in the laboratory by heating a mixture of sodium acetate, sodium hydroxide, and lime (CaO) in a hard glass or metal vessel, and collecting the

gaseous product over water. It may also be prepared by the interaction of aluminium carbide and water, thus: —

$$\underset{\text{Aluminium Carbide}}{Al_4C_3} + \underset{\text{Water}}{12\,H_2O} = \underset{\text{Methane}}{3\,CH_4} + \underset{\text{Aluminium Hydroxide}}{4\,Al(OH)_3}$$

Methane has no color, taste, or odor. It burns with a pale, bluish flame. A mixture of methane with oxygen or air explodes violently when ignited by a spark or flame. Terrible disasters occur in coal mines from this cause. The products of the explosion are carbon dioxide and water, thus: —

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Oxygen}}{2\,O_2} = \underset{\text{Carbon Dioxide}}{CO_2} + \underset{\text{Water}}{2\,H_2O}$$

The carbon dioxide, called choke damp or black damp by the miners, often suffocates those who escape from the explosion.

**Ethylene**, $C_2H_4$, or olefiant gas, is formed by the destructive distillation of wood and coal. It is usually prepared in the laboratory by heating a mixture of concentrated sulphuric acid and ethyl alcohol (*i.e.* ordinary alcohol), and collecting the gas over water. The essential change is represented thus: —

$$\underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Ethylene}}{C_2H_4} + H_2O$$

Ethylene is a colorless gas and has a pleasant odor. Its critical temperature is 9° C. and its critical pressure is 58 atmospheres, so it can be readily condensed to a liquid. The latter by evaporation in a vacuum produces a temperature as low as — 140° C. and is sometimes used to produce low temperatures. The gas burns with a bright, yellow flame, and is one of the essential illuminating ingredients of coal gas. When ethylene burns, the complete combustion is represented thus: —

$$\underset{\text{Ethylene}}{C_2H_4} + 3\,O_2 = \underset{\text{Carbon Dioxide}}{2\,CO_2} + \underset{\text{Water}}{2\,H_2O}$$

If mixed with oxygen in this proportion and ignited, the mixture explodes.

**Acetylene**, $C_2H_2$, is formed by the direct union of hydrogen and carbon when an electric arc is produced between two carbon rods in hydrogen gas. This method of formation, though not convenient, is interesting, because very few hydrocarbons have as yet been formed directly from their elements. A small quantity is present in coal gas. It is also formed by the incomplete combustion of coal gas, *e.g.* when the flame of a Bunsen burner strikes back and burns at the base. (See Bunsen Burner, below.) Acetylene is now prepared cheaply on a large scale by the interaction of calcium carbide and water, thus : —

$$\underset{\text{Calcium Carbide}}{CaC_2} + \underset{\text{Water}}{2\,H_2O} = \underset{\text{Acetylene}}{C_2H_2} + \underset{\text{Calcium Hydroxide}}{Ca(OH)_2}$$

Acetylene is a colorless gas, and, if impure, has an offensive odor. It is poisonous if breathed in large quantities, but much less dangerous than gases containing carbon monoxide. It is lighter than air, its density being about .92. Water at the ordinary temperature dissolves its own volume of the gas. Reliable tests show that acetylene does not act upon any common metal or alloy, though it forms explosive compounds with salts of metals, especially of copper. As a precaution, copper and brass are seldom used in large vessels containing or generating acetylene, though they might safely be used in small lamps.

The critical pressure is about 61 atmospheres and the critical temperature is about 35° C., so acetylene can be readily liquefied. Cylinders of liquid acetylene have exploded, causing loss of life and destruction of property, and its use in this form has been prohibited

in some localities. Under ordinary atmospheric pressure acetylene gas does not explode, but if subjected to a pressure of two or more atmospheres, it will explode by a shock or when a spark or flame is brought near it. A mixture of acetylene and air, if ignited, explodes. The mixture to be explosive, however, must contain a large per cent of acetylene (a condition hardly possible except from sheer carelessness, because the disagreeable odor reveals the presence of the gas). Acetylene gas, it is evident, must be used with the same precaution as any other illuminating gas.

Acetylene is found by analysis to contain only carbon and hydrogen combined in the ratio of 12 to 1 by weight. Its vapor density is .8125 (if $O_2=32$). Therefore its molecular weight is 26 and its formula is $C_2H_2$. The graphic formula of acetylene is usually written thus: $H-C\equiv C-H$.

**Acetylene as an Illuminant.** — Acetylene burns in the air with a luminous, smoky flame. But when air is mixed with the gas as the latter issues from a small opening, the mixture burns with a brilliant, white flame, which does not smoke. It is coming into use as an illuminant. The flame is almost like sunlight, hence by the acetylene flame most colors appear the same as in daylight. It is adapted for taking photographs, since its action closely resembles that of the sun. It is a diffusive light, and the flame is much smaller than an ordinary gas flame of the same lighting power (Fig. 37).

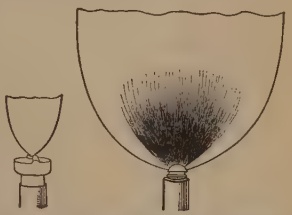


FIG. 37. — Relative size of acetylene and illuminating gas flames giving the same amount of light. The acetylene (smaller) flame consumes only one tenth as much gas an hour as the illuminating gas flame. (One half actual size.)

With a proper burner the combustion of acetylene is complete and may be represented thus: —

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O$$

Fig. 38. — Acetylene flame.

In most acetylene burners the gas issues from two small holes drilled at an angle, so that the jets strike each other and produce a flat flame (Fig. 38). Other holes, properly located, permit air to be drawn in mechanically by the acetylene as it rushes through the burner. The openings for the mixture are so fine that the flame cannot strike back and cause an explosion (Fig. 39).

Fig. 39. — Acetylene burner.

**Generation of Acetylene.** — The ease with which acetylene is generated can be shown by putting a little water in a test tube and then dropping in a small lump of calcium carbide. The gas bubbles through the liquid; after the action has gone on long enough to expel the air, the acetylene may be lighted by holding a burning match at the mouth of the tube. On a larger scale, the gas can be generated by putting the calcium carbide into a flask provided with a dropping funnel and delivery tube, and allowing water to drop *slowly* upon the carbide; the gas thus generated can be collected in bottles over water. There are two classes of commercial generators. In one, water is added to the carbide, but in the other the carbide drops into the water. The intense heat liberated when calcium carbide interacts with water decomposes acetylene; hence, a generator to be effective and safe should be constructed so that this heat will be absorbed. The first class of generators is dangerous, except when a small quantity of gas is desired, as on the lecture table or in a lantern. In the second class, a small amount of calcium carbide drops automatically into a large volume of water as fast as the gas is needed, thus insuring a pure, cool gas, and eliminating the danger of an explosion. A pound of calcium carbide yields about five cubic feet of acetylene gas. Acetylene dissolves in acetone, and cylinders in which considerable gas has been dissolved under pressure are used to furnish gas for automobile lanterns.

Acetylene is an endothermic compound, and several of its properties described above are due to its endothermal nature. It is formed from its elements with absorption of heat, and requires the temperature of the electric arc for its formation. If an electric arc is produced between two carbon electrodes in a vessel through which hydrogen is passed, acetylene is formed. Being endothermic, it explodes when subjected to a shock (if the gas is under a pressure of two or more

atmospheres), and the elements are re-formed with liberation of heat, thus: —

$$C_2H_2 = 2\,C + H_2 + 53{,}100 \text{ cal.}$$

The temperature of the acetylene flame is very high on account of the large amount of heat liberated by its combustion, the heat of combustion being about 310,000 cal.; the thermal equation for this change is —

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O + 310{,}000 \text{ cal.}$$

The brilliancy of the acetylene flame is largely due to its high temperature.

**Petroleum** is the source of numerous hydrocarbons. It is an oily liquid obtained from the earth in many parts of the world. In the United States the chief localities are Ohio, New York, Pennsylvania, West Virginia, Kentucky, Indiana, Colorado, Texas, and California. The immense deposits in Russia are in the Baku district on the Caspian Sea. Some is also found in Canada, India, Japan, and Austria.

Crude petroleum is an oily liquid, with an unpleasant odor. Its color varies from straw to greenish black, and most kinds are greenish in reflected light. It usually floats upon water. Its composition is complex, but all varieties are essentially mixtures of several liquid and solid hydrocarbons. American oils contain chiefly members of the paraffin series (*i.e.* methane series). Some varieties contain compounds of nitrogen and of sulphur.

In some localities the oil issues from the earth, but it is usually necessary to drill through rocks and insert a pipe into the porous rock containing the oil. At first the oil often "shoots" out of the well in tremendous volumes, owing to the pressure of the confined gas, but after a time a pump is needed to draw it to the surface. The oil is then forced by powerful pumps through large pipes to central points for storage or for delivery to refineries, which are often many miles from the oil well. This network of pipes in the eastern United States is over 25,000 miles long.

Some crude petroleum is used in making water gas (see below) and as fuel on locomotives and steamships, but most of it is separated into various commercial products. This process is called **refining**. The petroleum is cleaned by settling and filtration, and then distilled in huge iron vessels. The vapors are condensed as they pass through coiled pipes immersed in cold water. Certain products are obtained from the residue left in the still. (See below.)

The different distillates, which are collected in separate tanks, are further separated by redistillation and purified by special treatment. The commercial products obtained from the first distillation are cymogene, rhigolene, gasolene, naphtha, benzine, and kerosene. These liquids are mixtures of several different hydrocarbons. They are widely used as solvents, fuels, illuminants, and in making gas.

**Kerosene** is the well-known illuminating oil. Being the most valuable product from petroleum, it is carefully freed from inflammable liquids and gases, which might cause an explosion, and from tarry matter and semisolid hydrocarbons, which would clog the wicks of lamps. This is done by agitating it successively with sulphuric acid, sodium hydroxide, and water. Commercial kerosene must have a legal **flashing point**. Flashing point is "the temperature at which the oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface." The legal flashing point varies in different localities from 44° C. to 68° C.

From the residuum left in the still after the first distillation **lubricating oils**, **vaseline**, and **paraffin wax** are obtained by further treatment. Mineral lubricating oils have largely replaced animal and vegetable oils. Vaseline finds extensive use as an ointment. Paraffin wax is used to make candles, to waterproof paper, to extract oils from plants and flowers; also as a coating for many substances, thereby producing a smooth surface or facilitating slow combustion (as in certain matches). The final residue left in the retorts is coke. Hydrocarbons are often extracted from it, some is made into electric light carbons, and some is used as a fuel.

**The source of petroleum** is doubtful. According to some authorities it was produced by the decomposition or slow distillation of plants and animals. Recently it has been suggested that it resulted from the interaction of water and metallic carbides, especially iron

carbide, at great depths. It is not unlikely that several sources may be involved.

**Natural Gas** is a combustible gas, which issues from the earth in many places. Methane is the principal constituent of the mixture. It is used as a fuel for heating houses, generating steam, and manufacturing iron, steel, glass, brick, and pottery. In Ohio, Indiana, and other gas-producing regions of the United States, wells, like petroleum wells, are drilled for the escape of natural gas, which is distributed to consumers through pipes similar to those used for illuminating gas.

**Illuminating Gas.** — Besides acetylene there are other kinds of illuminating gas. Coal gas and water gas are the most common.

**Coal Gas** is made by distilling bituminous coal and purifying the volatile product. The hydrogen in the coal passes off partly as free hydrogen, and partly in combination with carbon as hydrocarbons and with nitrogen as ammonia. The ammonia, carbon dioxide, and sulphur compounds are regarded as impurities, and are removed as completely as possible before the gas is delivered to the consumer. The by-products are coke, gas carbon, tar, and ammoniacal liquor. The essential parts of a coal gas plant are shown in Figure 40.

The coal is distilled in air-tight ⌂-shaped retorts made of fire clay. The volatile products escape through a pipe, and bubble through water into the hydraulic main. Here some of the tar is deposited and the ammonium compounds are dissolved by the water that flows constantly through the main. This water is kept at a constant level and acts as a "seal" to prevent the gas from passing back into the retorts. The ammoniacal liquor and tar flow into separate wells. From the hydraulic main the gas, which is hot and impure, passes into the condenser. This is a long series of vertical iron pipes, so constructed that the gas must pass through the entire

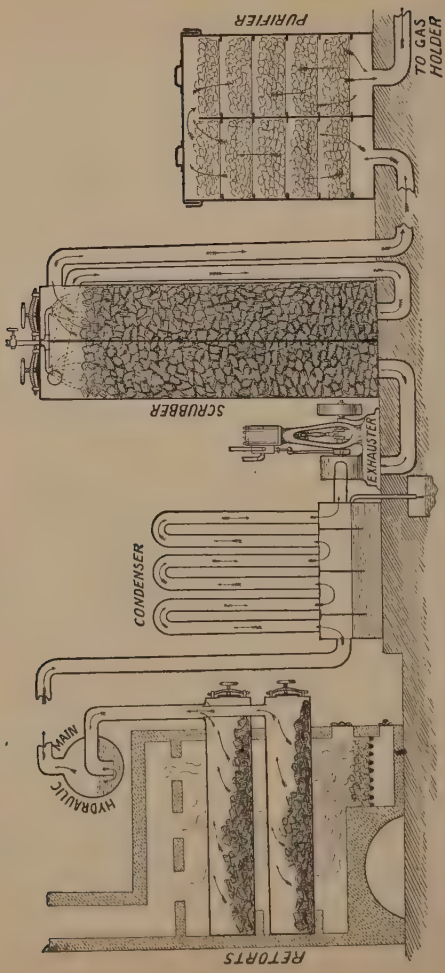



FIG. 40. — Apparatus for manufacturing coal gas.

length of the pipes, while the tar and ammoniacal liquor flow into the proper receptacles. The main object of the condenser is to cool the gas slowly and condense and remove the tar. An exhauster, in most plants, draws or forces the gas from the hydraulic main through the condenser into the scrubber and onward through the purifiers into the gas holder. The exhauster also reduces the pressure in the retorts and regulates the pressure in the holder. (See below.) From the exhauster the gas passes into the scrubber. Its purpose is to remove the remaining ammonia, part of the carbon dioxide and the hydrogen sulphide gas, and the last traces of tar. Scrubbers vary in construction. One form is a double tower filled with wooden slats or with trays covered with coke or pebbles over which ammoniacal liquor slowly trickles in the first part and pure water in the second. The gas enters at the bottom, meets the descending liquid, and is thoroughly washed. Another form widely used consists of a cylindrical vessel in which numerous wooden slats revolve in compartments and dip into ammoniacal liquor or water at the bottom. The liquid forms a film on the slats and absorbs the ammonia and other gases, while the resulting solution mixes with the liquor at the bottom and flows into the proper well. Sometimes a separate tar extractor is connected with the scrubber. This is a tower filled with perforated plates, which catch and remove the tar mechanically as the gas passes through into the scrubber. From the scrubber the gas passes into the purifiers. Their chief purpose is to remove the remaining carbon dioxide and sulphur compounds. They are shallow, rectangular iron boxes provided with slat frames loosely covered with lime. In some plants iron oxide is used as the purifying material.

The purified gas next passes through a large meter, which records its volume, into a gas holder. The holder is an enormous, cylindrical, iron tank in which the gas is stored. Weights and the pressure from the exhauster so balance it that it exerts just enough pressure to force the gas through the pipes to the consumer.

A ton of good coal yields about 10,000 cubic feet of gas, 1400 pounds of coke, 120 pounds of tar, 20 gallons of ammoniacal liquor, and a varying amount of gas carbon. The coke, which remains in the retorts after distillation, is sold as fuel. The tar, or coal tar as it is often called, collected from the hydraulic main and condenser, is a thick, black, foul-smelling liquid. Some is used for preserving timber, making tarred paper and concrete, and as a protective paint. Most of it is now separated by distillation into its more important

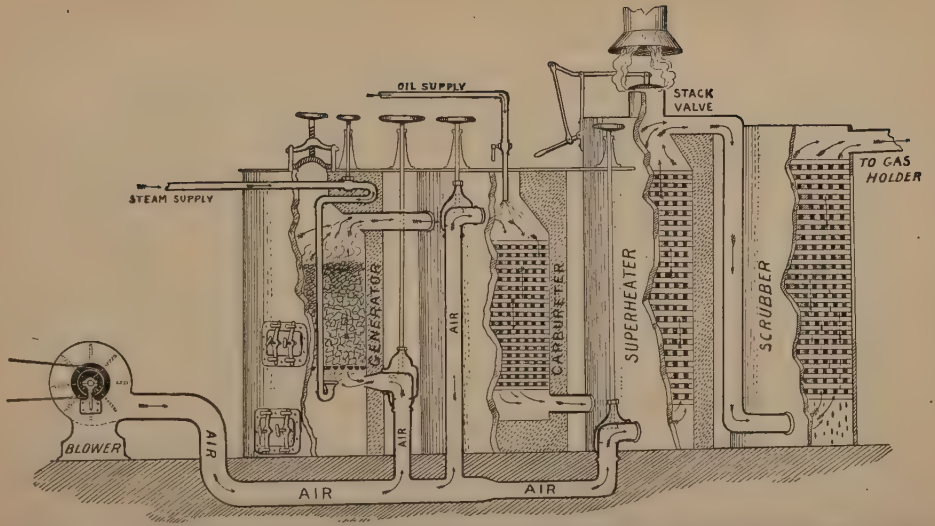



FIG. 41. — Apparatus for manufacturing water gas. In many plants a seal box (similar to the seal in the hydraulic main) is placed between the superheater and scrubber to prevent the backward flow of the gas.

components, especially benzene ($C_6H_6$). The ammoniacal liquor from the hydraulic main, condenser, and scrubber is the source of ammonia and its compounds. Gas carbon is the hard deposit which collects on the inside of the retort, and is used in the electrical industries. (See Gas Carbon.)

**Water Gas** is mainly a mixture of hydrogen and carbon monoxide. It is made by forcing steam through a mass of hot anthracite coal and mixing the gaseous product with hot gases obtained from oil. The essential parts of the apparatus are shown in Figure 41. .

Air is forced through the coal fire in the generator, and the hot gases which are produced pass down the carburetor, up into the superheater, and escape through its top into the open air. This operation lasts about four minutes, and is called the "blow." It heats the fire brick inside the carburetor and superheater intensely hot, air often being forced in to raise the temperature. The air valves and the top of the superheater are now closed, and the "run" begins, which lasts about six minutes. Steam is forced into the generator at the bottom. In passing through the mass of incandescent carbon the steam and carbon interact thus: —

$$\underset{\text{Carbon}}{C} + \underset{\text{Steam}}{H_2O} = \underset{\substack{\text{Carbon}\\\text{Monoxide}}}{CO} + \underset{\text{Hydrogen}}{H_2}$$

This mixture of hydrogen and carbon monoxide burns with a feeble though hot flame, and is sometimes used as fuel. Before this mixture can be used as an illuminating gas it must be enriched with gases which are illuminants. Therefore, the mixed gases pass to the top of the carburetor, where they meet a spray of oil. And as the gaseous mixture passes down the carburetor and up the superheater, the hydrocarbons of the oil are transformed by the intense heat into hydrocarbons which do not liquefy when the gas is cooled. The addition of hydrocarbons is called carbureting. From the superheater the water gas passes through the purifying apparatus into a holder.

Water gas itself is seldom burned alone, but is usually mixed with 60 or 70 per cent of coal gas. This mixture is popularly called "illuminating gas." Owing to the high

percentage of carbon monoxide, water gas and gases containing it are poisonous. (See Carbon Monoxide.)

**Characteristics of Illuminating Gases.** — Both coal gas and water gas have a disagreeable odor. They are mixtures, and vary in composition with the coal used, the temperature reached, and the degree of purification attained. The following table shows the average: —

Composition of Illuminating Gases

| Constituents | Coal Gas | Water Gas |
|---|---|---|
| Ethylene (and other illuminants) . . . . | 5.0 | 16.6 |
| Methane . . . . . | 34.5 | 19.8 |
| Hydrogen . . . . . | 49.0 | 32.1 |
| Carbon monoxide . . . . . | 7.2 | 26.1 |
| Carbon dioxide . . . . . | 1.1 | 3.0 |
| Nitrogen . . . . . | 3.2 | 2.4 |

Both kinds of illuminating gas may contain a little oxygen and traces of ammonia and hydrogen sulphide gas. Nitrogen and the last portions of carbon dioxide are impurities not easily removed. Methane, hydrogen, and carbon monoxide burn with a feeble (non-yellow) flame, and are often called diluents; they furnish heat, but no light.

The **luminosity** of illuminating gas depends mainly upon the presence of the hydrocarbons that contain a relatively large proportion of carbon. The most important illuminants in coal gas and water gas are ethylene (and analogous hydrocarbons in the same series), acetylene, and benzene ($C_6H_6$). The utility of an illuminating gas depends upon its luminosity. This property is measured by a photometer and is expressed in "candles," or **candle power.** The determination of candle power is made by comparing the light produced by burning the gas in a standard burner

at the rate of five cubic feet an hour with the light produced by a standard wax candle burning at the rate of 120 grains (7.77 gm.) an hour. If the gas flame is 20 times brighter than the candle flame, then the candle power of the gas is 20. The candle power of ordinary coal gas is about 17, and that of water gas is about 25. Ordinary illuminating gas has a candle power of about 20, since it usually is a mixture of coal gas and water gas.

**Flame.** — Chemical action, as we have already seen, is often accompanied by light. Sometimes the light is merely a glow, as in the case of burning charcoal, or a shower of sparks, seen when iron burns in oxygen, or a mere flash, displayed by an explosion of hydrogen and oxygen. But when the interacting substances are gases or vapors from volatilized liquids or solids, the chemical change is accompanied by a more or less quiet and continuous light. The term *flame* is commonly applied to such a light, though a flame is really a series of chemical changes in which the gases interact at such a temperature that light is produced. Popularly, a flame is a gas burning in the air, *i.e.* the gas or some of its elementary constituents are combining with the oxygen of the air. But since the flame is due primarily to the chemical combination of the oxygen of the air and the gas, it is immaterial where the actual change takes place. Ordinarily, the gas burns in the surrounding air, but the flame is produced just as truly, though not so conveniently, in a vessel of illuminating gas, provided, of course, air is supplied. This change of atmospheres, so to speak, is shown by a simple experiment (Fig. 42). The lamp chimney *B* is filled with illuminating gas through the bent tube *D*, and its escape is temporarily prevented by closing the opening in the asbestos cover *A*. The gas is lighted at the lower end of the tube *C*, and when the hole in *A* is uncovered,

the flame rises in *C* and continues at the end within the chimney as long as air is drawn up through *C* and gas supplied through *D*. The unconsumed illuminating gas escapes through the hole in A, and if ignited, burns as shown in the figure. Chemically both flames are alike. The outer flame is in an atmosphere of air, while the inner flame is in an atmosphere of illuminating gas; but both are due to the combination of oxygen with the elementary constituents of the illuminating gas.

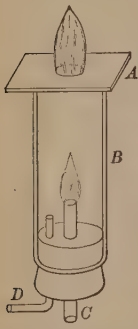


FIG. 42. — Combustion in illuminating gas and in air.

In an illuminating gas flame the gas itself is burning in the air. In a lamp flame the burning gas comes from the oil which is drawn up through the wick and then volatilized by the heat. Similarly, in a candle flame the burning gas comes from the melted wax. The flame produced by most burning hydrocarbons is luminous and has a yellowish white color.

**Luminous Flames.** — The luminous hydrocarbon flame has several distinct parts, and the structure of the flame is essentially the same, whether produced by burning illuminating gas, kerosene oil, or candle wax. The candle flame may be taken as the type. An examination of the enlarged vertical section shown in Figure 43 reveals four somewhat conical portions. (1) Around the wick there is a black cone (*A*), filled with combustible gases formed from the melted wax. They do not burn because no oxygen is present. With a glass tube of fine bore it is possible to draw off these gases from a large flame and light them at the upper end of the tube. (2) Around the lower part of the dark cone is a faint bluish cup-shaped part (*B*, *B*). It is the lower portion of the exterior cone where complete

combustion of the gases occurs, since plenty of oxygen from the air reaches this portion. (3) Above the dark cone is the luminous portion (*C*). It is the largest and most important part of the flame. It is usually spoken of as "the

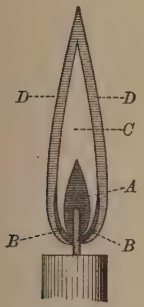



FIG. 43. — Typical candle flame.

FIG. 44. — Paper charred by a candle flame.

flame." Combustion is incomplete here, because little or no oxygen can pass through the exterior cone. The temperature is high, however, and the hydrocarbons undergo complex changes. Acetylene is probably formed. The most characteristic change is the liberation of small particles of carbon. This liberated carbon, heated to incandescence by the burning gases, makes the flame luminous. The carbon glows but does not burn up, because little or no oxygen is present. A piece of crayon or glass rod held in this part of the flame is at once coated with soot, which consists of very fine particles of carbon. (4) The exterior cone (*D*, *D*) is almost invisible. Here the combustion is complete, because the oxygen of the air changes all the carbon into carbon dioxide. That this is the hottest region of the flame may be easily shown by pressing a piece of stiff white paper for an instant down upon the flame almost to the wick.

The paper will be charred by the hot outer portion of the flame, as shown in Figure 44.

These four portions may be found in all luminous hydrocarbon flames, whatever the shape. An ordinary gas flame is flattened by forcing the gas through a narrow slit in the burner tip, so that the flame will give more light. The blue part is easily seen, however, when the gas flame is turned low or looked at through a small opening; the dark and yellow parts are always visible — the latter being intentionally enlarged. The flat or circular flame of an oil lamp likewise presents the same characteristics.

The gaseous products of the combustion of hydrocarbons are water vapor and carbon dioxide. A bottle in which a candle is burning has, at first, a deposit of moisture on the inside; and if the candle is removed and limewater added, the presence of carbon dioxide is shown by the cloudiness of the limewater. The oxygen needed by the burning hydrocarbons is obtained from the air. If not enough oxygen is present, the flame smokes, *i.e.* the carbon is thrown off into the air before the particles are heated hot enough to glow. All oil lamps are so constructed that air enters the burner below the flame. Large oil lamps have a central opening through which a large volume of air passes up inside the circular flame. Otherwise the lamp would burn with a very smoky flame.

The luminosity of hydrocarbon flames is affected by other factors besides the presence of glowing carbon. One of these is temperature. Gases cooled before being burned give very poor light. A candle flame may be cooled enough to extinguish it. Thus, if a coil of copper wire is lowered upon a candle flame, the flame smokes, loses its yellow color, and finally goes out; but if a coil of hot wire is used, the flame burns unchanged. Gases, as well as solids and liquids, have a kindling temperature, *i.e.* a temperature to which they

must be heated before they "catch fire." This temperature differs with different substances. As we lower the temperature of gases burning with a luminous flame, their luminosity decreases, and below their kindling point they will not burn. The density of the gases in the flame and of the atmosphere itself likewise modifies luminosity. The flame of a candle was found by experiment to be smaller on the top of Mont Blanc than at the base.

Not all luminous flames are hydrocarbon flames. Thus, magnesium burns with a brilliant flame. Its luminosity is due to the incandescence of solid particles of magnesium oxide. Similarly, the bright flame of burning phosphorus is accounted for by the incandescent particles of solid phosphorus pentoxide. Most luminous flames contain solid particles, though in a few cases luminosity is caused by the combustion of gases under pressure, no solid particles whatever being produced.

**Non-Luminous Flames.** — Not all flames are luminous. The hydrogen flame is almost invisible in air and oxygen, but pale blue in chlorine. The flames of carbon monoxide and methane are also a faint blue. The most common non-luminous flame is the Bunsen flame.

**The Bunsen Burner and its Flame.** — When illuminating gas is mixed with air before burning, and the mixture burned in a suitable burner, a flame is produced which is non-luminous and very hot. The temperature of the hottest part is about 1500° C. This flame deposits no carbon, since its products are entirely gaseous. Such a flame is called the Bunsen flame, for it was first produced in a burner devised by the German chemist Bunsen. This burner is constantly used in chemical laboratories as a source of heat, and modified forms have numerous uses. One form, for example, furnishes the heat in the gas range used for cooking.

The parts of a typical Bunsen burner are shown in Figure 45. The gas enters the base and escapes through a very small opening into the long tube, which screws down over this opening. At the lower end of the long tube there are two holes, through which air is drawn by the gas as it rushes out of the small opening. The gas and air mix as they rise in the tube, and this mixture of air and gas burns at the top of the long tube. The size of the air holes at the bottom of the long tube may be changed by a movable ring, thus varying the volume of the entering air. When the holes are open, the typical non-luminous, hot Bunsen flame is formed. The combustion of the constituents of the hydrocarbons is practically complete. The non-luminous flame is free from soot, therefore apparatus heated by this flame is not blackened. The Bunsen flame can be made luminous by closing the air holes or by introducing fine particles into the flame, — such as charcoal dust, finely divided metals, and sodium compounds.

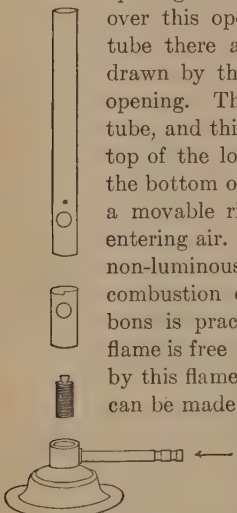


Fig. 45. — Parts of a typical Bunsen burner.

It was formerly believed that the non-luminous character of the Bunsen flame is solely due to the complete combustion of the carbon by the oxygen of the entering air. Recent experiments have shown, however, that the result is partly due to the diluting action of the nitrogen.

The gas burns at the top of the tube, not inside, because the proper mixture of gas and air flows out more quickly than the flame can travel back through the tube to the small exit. If the gas supply is slowly decreased, the flame becomes smaller, disappears with a slight explosion, and burns at the exit inside the tube. A sudden draft of air, too large

holes at the lower end of the tube, or too low gas pressure also may cause the flame to " strike back," as this action is called. This change is due to the fact that the tube contains an explosive mixture of air and illuminating gas, through which the flame travels downward faster than the mixture escapes from the tube. This modified flame has a pale color and disagreeable odor, and deposits soot.

The Bunsen flame has many characteristic properties. Its color is bluish, and the different cones have different tints. There are really three cones: (1) the blue or greenish inner one of unburned gases; (2) the very faint blue middle one; (3) and the outer one, which is a pale blue, and represents the blue cone in the candle flame. The middle and outer cones are not always easily distinguished; so for all practical purposes it is convenient to divide the flame into two parts, — an inner cone of unburned gases and an outer cone in which all the carbon is consumed. Combustible gases may be drawn off by a tube from the inner cone and ignited. A match laid for an instant across the top of the tube is charred only at the two points where it touches the outer cone; and a sulphur match suspended by a pin across the top of an unlighted burner is not kindled until several minutes after the gas is first lighted.

A piece of wire gauze pressed down upon the Bunsen flame shows a dark central portion surrounded by a luminous ring. The flame is beneath the gauze, although the gas passes freely through it and escapes. If the gas is extinguished and then relighted above the gauze, it will burn above but not beneath (Fig. 46). The gauze cools the gas below its kindling tem-

Fig. 46. — The effects of wire gauze on a Bunsen flame.

perature. The miner's safety lamp invented by Davy depends upon this last principle. It is an oil lamp surrounded by a cylinder of fine wire gauze (Fig. 47). When taken into a mine where there are explosive gases (such as methane — see Methane), the flame continues to burn inside, though its size and color change. The gas often enters the lamp and burns inside, but the flame within does not ignite the gases without because the wire gauze keeps them cooled below their kindling temperature. Hence an explosion is often prevented. When miners notice changes in the lamp flame, they usually seek a safe place.

FIG. 47. — One form of Davy's safety lamp.

**Oxidizing and Reducing Flames.** — The outer portion of the Bunsen flame is called the oxidizing flame, because here the oxygen is freely given to substances. The inner portion is called the reducing flame, because here the hydrocarbons withdraw oxygen. A sketch of the general relation of these flames is shown in Figure 48. *A* is the most effective part of the oxidizing flame, and *B* of the reducing flame. At *A* metals are oxidized, and at *B* oxygen compounds are reduced. Sometimes a long tube with a small opening at one end, called a blowpipe, is used to produce these flames. Another tube with a flattened top is put inside the burner to produce a luminous flame. The tip of the blowpipe rests in or near this flame, and if air is gently and continuously blown through the blowpipe, a long, slender flame

FIG. 48. — The oxidizing (*A*) and reducing (*B*) flames.

is produced, called a blowpipe flame (Fig. 49). It is like the Bunsen flame as far as its oxidizing and reducing properties are concerned. The blowpipe is used in the laboratory and by jewelers and mineralogists. On a large scale the blowpipe flame is used to reduce or oxidize ores. (See Compound Blowpipe.)

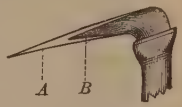



FIG. 49. — Blowpipe flame, showing oxidizing (*A*) and reducing (*B*) parts.

The Bunsen flame has recently been utilized in producing the Welsbach light. The non-luminous flame heats an inverted bag or mantle of oxides of thorium and cerium, and the mantle glows with an intense light. The candle power varies from 40 to 100. This form of burner is widely used because it produces a brilliant light.

### PROBLEMS

1. Calculate the percentage composition of (*a*) methane ($CH_4$), (*b*) ethylene ($C_2H_4$), and (*c*) acetylene ($C_2H_2$).

2. What weight of oxygen is needed for the complete combustion of 4 gm. of ethylene? (Equation is $C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O$.)

3. What is the simplest formula of a compound having the composition H = 7.69 and C = 92.3?

4. Calculate the molecular formula of a compound having the vapor density 2.425 (referred to oxygen) and the composition C = 92.3 and H = 7.69.

5. If a hydrocarbon contains 80 per cent carbon, and a liter of it weighs 1.346 gm., what is its formula?

6. A volatile liquid contains 37.5 per cent of carbon, 50 per cent of oxygen, and 12.5 per cent of hydrogen; a liter of the vapor weighs about 16 times that of hydrogen. What is the molecular formula?

7. A gaseous hydrocarbon contains 85.71 per cent of carbon; its density referred to oxygen is .875. What is (*a*) its simplest formula and (*b*) its molecular formula?

# CHAPTER XVII

## Other Carbon Compounds

**Introduction.** — It was formerly believed that starch, sugar, and other compounds obtained from plants and animals were produced by the influence of some mysterious vital force. Such compounds were called **organic**, because of their connection with living things, *i.e.* with bodies having organs; and they were sharply distinguished from **inorganic** or mineral compounds obtained from the earth's crust. This distinction prevailed until Wöhler, in 1828, prepared urea — a distinct organic compound — from inorganic substances. Since then the barrier between the two classes of compounds has been completely removed. It is now believed that compounds of carbon, whatever their source, are subject to the laws that govern all other compounds. The terms *organic* and *inorganic* are still used, though they have lost their original narrow meaning. Carbon forms a vast number of compounds which are related to each other, and which differ from most compounds of other elements. It is convenient, therefore, to distinguish these compounds by the term *organic* and to study them under the comprehensive title of Organic Chemistry or the Chemistry of Carbon Compounds. Several organic compounds have already been discussed in the chapter immediately preceding. A few typical compounds only can be considered in the present chapter.

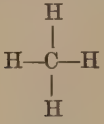
**Composition of Organic Compounds.** — The number of organic compounds is very large, but they contain only a few elements — seldom more than four or five. Hydrocarbons,

as already stated, contain only carbon and hydrogen. Vegetable substances, typified by starch, sugar, and fruit acids, contain carbon, hydrogen, and oxygen. Animal substances, like hair, albumen, gelatine, and muscle generally contain nitrogen as well as carbon, hydrogen, and oxygen; some also contain sulphur or phosphorus. Artificial organic compounds, like dyestuffs and medicines, may contain any element, especially chlorine, iodine, and certain metals.

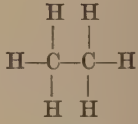
The number and complexity of organic compounds are due to several facts. (1) Atoms of carbon, unlike those of most elements, have power to unite with themselves. (2) Atoms of different elements can be introduced into carbon compounds. Sometimes these atoms are simply added, sometimes they replace other atoms, thus producing an endless number of addition and substitution products. (3) The same number of atoms may arrange themselves differently, thereby producing isomeric compounds having different properties. (4) Organic compounds contain radicals. These **radicals** are groups of atoms analogous to hydroxyl (OH) and ammonium ($NH_4$), and like these radicals they exist only in combination. They act chemically like single atoms and pass from one compound to another without decomposition. The radical $C_2H_5$ is called **ethyl**. It is present in many organic compounds, and its presence in ordinary alcohol gives rise to the scientific name, ethyl alcohol. **Methyl** ($CH_3$) is another important radical, and **phenyl** ($C_6H_5$) is especially common in the benzene series of organic compounds.

**Structure of Organic Compounds.** — An extensive study of the properties of organic compounds has revealed many facts about their **constitution**, *i.e.* the structure of their molecules. Relatively little is known about the shape, size, etc., of molecules, but much is known about the grouping of atoms and of radicals in the molecules. These facts, which are

ascertained by experiment and are often too complex to be expressed briefly, may be represented by suitable formulas. Thus, the ordinary or **empirical formula** of alcohol is $C_2H_6O$. But this formula tells nothing about the relation these atoms bear to each other. Experiment shows that (1) one hydrogen atom acts differently from the other five, and (2) one hydrogen atom is always associated with the oxygen atom in chemical changes. Hence, the formula $C_2H_5 . OH$ expresses more fully these facts. Such a formula is called a **rational** or **constitutional formula**. Sometimes constitution is expressed by a **graphic** or **structural formula**. Thus, methane and ethane have the graphic formulas: —

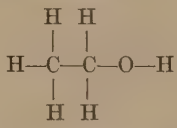


Methane



Ethane

In these diagrams the single lines represent a valence of one — nothing else, and the number of lines connected with each atom is equal to the valence of the element in the compound. The lines are sometimes called bonds or links, but they are not intended to represent attraction or any other force. The graphic formula of ethyl alcohol is : —



This is not an arbitrary arrangement; the facts mentioned above necessitate this general configuration.

**Classification of Organic Compounds.** — Organic compounds are divided and subdivided into many classes, mainly

for the purposes of study. The most common classes are: (1) Hydrocarbons; (2) Alcohols; (3) Aldehydes; (4) Ethers; (5) Acids; (6) Esters; (7) Fats, glycerine, and soap; (8) Carbohydrates; (9) Benzene and its derivatives; (10) Cyanogen and its derivatives. Some compounds are so closely related that they really belong to several of these groups, while a few common ones are excluded.

### Hydrocarbons

Three of these compounds of carbon and hydrogen have been fully considered in Chapter XVI. The chief facts and fundamental principles recorded there may be profitably reviewed by the student at this point. Other hydrocarbons will be discussed under Benzene (see below).

Two important substitution products of methane are chloroform ($CHCl_3$) and iodoform ($CHI_3$). Chloroform is a heavy, sweet liquid. It is made by treating alcohol or acetone with bleaching powder, and is used as an anæsthetic, *i.e.* to produce unconsciousness in surgical operations. Iodoform is a yellow, disagreeable smelling solid. It is made by treating alcohol or acetone with iodine and sodium carbonate, and is used as an antiseptic, *i.e.* as a dressing to protect wounds from the harmful action of germs.

### Alcohols

Ordinary or ethyl alcohol is the best-known member of this group. It is often called simply alcohol. There are many alcohols analogous to ethyl alcohol, but the only other important one is methyl alcohol.

The alcohols may be regarded as hydroxides of certain radicals, viz. ethyl, methyl, propyl, etc.[1] For example, ethyl alcohol is ethyl hydroxide, and may be considered as formed by replacing one hydrogen atom of ethane ($C_2H_6$) by one hydroxyl group (OH). Again,

[1] The names of these and similar radicals are derived from the name of the corresponding hydrocarbon. Thus, *methyl* from *methane*, *ethyl* from *ethane*, *propyl* from *propane*.

alcohols are analogous to metallic hydroxides, in which the metal is replaced by a radical, thus: —

| $C_2H_5.OH$ | $NaOH$ |
|---|---|
| Ethyl Hydroxide | Sodium Hydroxide |

Alcohols and metallic hydroxides have some properties in common. Thus, both form salts with acids. With acetic acid, sodium hydroxide forms sodium acetate, while alcohol forms ethyl acetate. (See Esters.)

**Methyl Alcohol**, $CH_3.OH$, is a colorless or slightly yellowish liquid, much like ordinary alcohol. It boils at about 66° C., and burns with a pale flame which deposits no soot. It intoxicates, and if concentrated is poisonous. It mixes with water in all proportions. It is cheaper than ethyl alcohol, and is used as a solvent for fats, oils, and shellac, and in the manufacture of varnishes and dyestuffs. Methyl alcohol is often called **wood alcohol** or wood spirit, because it is one of the products obtained by the dry distillation of wood. (See Charcoal.)

**Ethyl Alcohol**, $C_2H_5.OH$, is a colorless, volatile liquid, having a burning taste and a pleasant odor. It is lighter than water, its specific gravity being about 0.8. It boils at about 78° C. Alcohol mixes with water in all proportions. The ordinary commercial variety contains about 95 per cent of alcohol. Pure or **absolute alcohol** is obtained by removing the remaining water with lime and dehydrated copper sulphate. **Denatured alcohol** is a mixture of 100 parts ethyl alcohol, 10 parts methyl alcohol, and a small proportion of benzine or pyridine (or a similar mixture); it is not taxed, and in its legalized forms is used as a cheap substitute for ordinary alcohol. It cannot be used as a beverage on account of the disagreeable taste, but is suitable for industrial uses. Alcohol is an excellent solvent for gums, oils, and resins, and is therefore extensively used in the manufacture of varnishes, essences, extracts, tinctures, perfumes,

and medicines. Many organic compounds, as ether and chloroform, are prepared from alcohol. Some vinegar is made from alcohol. In museums alcohol is used to preserve certain specimens. Alcohol is manufactured by the fermentation of sugars and starches.

**Fermentation** is a general term for the chemical changes caused by compounds secreted by **ferments**. The latter are minute living organisms; the compounds they secrete are called **enzymes**. The process and essential products vary with the nature of the ferment. The important kinds of fermentation are alcoholic, acetic, and lactic, and the characteristic products are alcohol, acetic acid, and lactic acid. **Alcoholic fermentation** is caused by the enzyme secreted by ordinary yeast. When yeast is added to a solution of glucose, maltose, or any other fermentable sugar, the yeast plants multiply rapidly. The changes are numerous and complex, but the main products resulting from the action of the enzyme from the yeast upon the sugar are alcohol and carbon dioxide, thus: —

$$\underset{\text{Glucose}}{C_6H_{12}O_6} = \underset{\text{Alcohol}}{2\,C_2H_6O} + \underset{\text{Carbon Dioxide}}{2\,CO_2}$$

Commercial alcohol is made from starch. The starch is changed into maltose, etc., by an enzyme called diastase, in the malt, and the maltose is changed into alcohol and carbon dioxide by an enzyme in the yeast. Wine, beer, and distilled liquors are essentially mixtures of alcohol and water. They differ mainly in their proportion of alcohol. The particular flavor is due to small quantities of different substances which are intentionally added, obtained from the raw materials, or formed by special processes of manufacture. Beer contains from 3 to 7 per cent of alcohol, wines from 6 to 20, rum, brandy, and whisky from 40 to 60 or more per cent.

### Aldehydes and Ketones

The important members of this twofold group are formic aldehyde (or formaldehyde) and acetone.

**Formaldehyde**, $CH_2O$, is a gas, but is used only in solution. It has a penetrating odor. The commercial solution sold as **formalin** contains 40 per cent of formaldehyde. Large quantities of formaldehyde are used in the manufacture of dyestuffs and fuming nitric acid, as a food preservative, and disinfectant. When used for the last purpose, the solution is vaporized in a special apparatus and the vapors conducted into the infected room. It is a convenient and efficient disinfectant.

**Acetone**, $C_3H_6O$, is a colorless liquid which has an ethereal odor. It boils at about 56° C. and mixes in all proportions with water, alcohol, and ether. It is used as a solvent for fats, oils, and waxes, and in the preparation of smokeless powders and certain organic compounds. Acetone is one of the products obtained by the dry distillation of wood. (See Charcoal.)

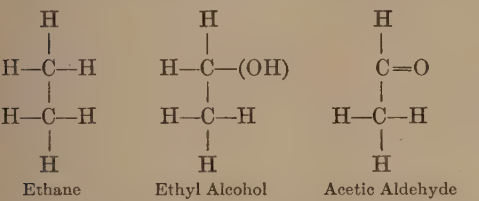
### Ethers

Ordinary or ethyl ether is the best-known member of this group.

**Ethyl Ether**, $C_4H_{10}O$, is a colorless, volatile liquid, with a peculiar, pleasing taste and odor. It boils at 35° C., and the vapor is very inflammable. The liquid should never be brought near a flame. It is somewhat soluble in water, and it also dissolves water to a slight extent. It mixes with alcohol in all proportions. It is a good solvent for waxes, fats, oils, and other organic compounds. Its chief use is as an anæsthetic. Ether is manufactured by distilling a mixture of ethyl alcohol and sulphuric acid in the proper proportions. Hence the name, ethyl or sulphuric ether.

## Acids

This large class of compounds is divided into several series, one of the most important of which is the **acetic** or **fatty series.** Its best known member is acetic acid; several of the higher members occur in fats and oils. These acids are closely related to hydrocarbons, alcohols, and aldehydes, as may be seen by the following formulas: —




The characteristic radical of organic acids is COOH (or O=C—O—H), and is called carboxyl.

**Acetic Acid,** $C_2H_4O_2$ or $CH_3.COOH$. This is the most common organic acid. It is manufactured on a large scale by the dry distillation of wood. The dark red watery distillate, which is called **pyroligneous acid**, contains about 10 per cent of acetic acid, besides methyl alcohol and acetone. This distillate is neutralized with lime or sodium carbonate, and the acetate formed is then decomposed and distilled with sulphuric acid. The acetic acid which condenses in the receiver may be further purified by distilling it with potassium dichromate and then filtering through charcoal. Sometimes the pyroligneous acid is distilled without neutralizing; the distillate is then dilute, impure acetic acid, and is known as **wood vinegar**. If sodium acetate, prepared as described above, is fused and then distilled with concentrated sulphuric acid, the product is very concentrated acetic acid.

It is called **glacial acetic acid**, because at about 17° C. it becomes an icelike solid.

Commercial acetic acid is a water solution containing about 30 per cent of pure acetic acid. It is a colorless liquid, having a pleasant odor and a sharp taste. It is a weak acid, a normal solution at 18° C. being dissociated to the extent of about .4 per cent into the ions $H^+$ and $C_2H_3O_2^-$. It mixes with water and alcohol in all proportions, and like alcohol is an excellent solvent for many organic substances. Recently, it has begun to replace alcohol as a solvent for many drugs.

Acetic acid is used to prepare acetates, dyestuffs, medicines, white lead, and in the manufacture of vinegar.

**Vinegar** is dilute, impure acetic acid. It is prepared by oxidizing dilute alcohol, the essential change being represented thus: —

$$\underset{\text{Alcohol}}{C_2H_6O} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Acetic Acid}}{C_2H_4O_2} + \underset{\text{Water}}{H_2O}$$

The transformation is accomplished by fermentation. (1) When beer, weak wines, or cider are exposed to the air, they slowly become sour, owing to the conversion of alcohol into acetic acid. The change is caused by the presence and activity of a ferment, known as *mycoderma aceti*, or "mother of vinegar." Strong wines and pure dilute alcohol do not become sour, because the ferment cannot live in such liquids. (2) Fruit juices slowly ferment when exposed to the air (which always contains the organisms necessary for the chemical transformations), forming alcohol first and finally vinegar. Cider vinegar is made this way. (3) In the "quick vinegar process," impure dilute alcohol is oxidized to acetic acid by exposing it to an excess of air. The operation is conducted in tall vats or casks filled with beechwood shavings soaked in strong vinegar. Holes at the bottom and top allow air to enter and escape freely. The alcoholic solution is introduced at the top, trickles through the shavings, and collects at the bottom. In its passage it comes in contact with the ferment and oxygen, and is partially converted into vinegar. The operation is repeated until the change is complete. Thus prepared, the vinegar lacks the flavor, odor, and color of cider vinegar, but these deficiencies may be artificially supplied.

**Acetates.** — Acetic acid is a monobasic acid, and forms only one series of salts — the **acetates.** They are prepared, like other salts, by the interaction of the acid and carbonates, hydroxides, metals, etc. The metallic acetates are usually crystalline solids, which readily yield acetic acid when treated with sulphuric acid. Most of them contain water of crystallization, and several are poisonous.

Acetates have many applications. **Sodium acetate,** $NaC_2H_3O_2 . 3\,H_2O$, is a white crystalline solid, used in preparing pure aectic acid and in the manufacture of dyestuffs. **Lead acetate,** $Pb(C_2H_3O_2)_2$, is a white crystalline solid, used in dyeing and in making a yellow pigment. Its sweet taste led to the common name of "sugar of lead." **Aluminium acetate,** $Al(C_2H_3O_2)_3$, is not known in the pure state, but an impure solution, known as "red liquor," is extensively used in dyeing and in calico printing. **Iron acetates** are sold in solution as a complex black liquid, known as "iron liquor," which is used in dyeing black silks and cottons, and in calico printing. (See Mordants.) A complex copper acetate, $2\,Cu(C_2H_3O_2)_2 + CuO$, called **verdigris,** is used in making blue paint. Another complex acetate of copper and arsenic is **Paris green;** it is used to kill potato bugs and other insects which injure vegetation.

**Other Organic Acids** which are important are oxalic, lactic, malic, tartaric, and citric.

*Oxalic Acid,* $C_2H_2O_4$, occurs as a salt in rhubarb and sorrel. It is manufactured on a large scale by heating sawdust with potassium hydroxide, and treating the residue first with lime and then with sulphuric acid. Oxalic acid is a white solid, very soluble in water, from which it crystallizes with two molecules of water of crystallization ($C_2H_2O_4 . 2\,H_2O$). It is very poisonous. It is dibasic and forms several useful salts. The acid and some of its salts decompose iron rust and inks containing iron, and are often used to remove such stains from cloth. The acid and its salts are also used in dyeing, calico printing, photography, in making dyestuffs, and as an ingredient of mixtures for cleaning brass and copper.

*Tartaric Acid,* $C_4H_6O_6$, occurs as the acid potassium salt ($HKC_4H_4O_6$) in grapes and other fruits. During the fermentation of grape juice, impure acid potassium tartrate is deposited in the casks. From this **argol** or crude **tartar** the acid itself is prepared by treating the raw product successively with chalk and sulphuric

acid. Tartaric acid is a white crystalline solid, soluble in water and alcohol. It is used in dyeing, and as one ingredient of Seidlitz powders. In these and similar mixtures it serves to decompose the other ingredient, which is a carbonate. (See Sodium Bicarbonate.)

Tartaric acid is dibasic and forms two classes of salts. Purified acid potassium tartrate obtained from argol is commonly known as **cream of tartar** ($HKC_4H_4O_6$). It is extensively used in the manufacture of baking powders. These, as a rule, are essentially mixtures of cream of tartar, sodium bicarbonate ($HNaCO_3$), and a little starch. When moistened by dough, the baking powder dissolves, the acid salt and the carbonate interact and liberate carbon dioxide. This gas escapes slowly through the dough, thereby puffing it up and making it porous. (See Sodium Bicarbonate.) **Tartar emetic** is potassium antimonyl tartrate ($KSbOC_4H_4O_6$). It is used as a medicine and to some extent in dyeing. Rochelle salt is potassium sodium tartrate ($KNaC_4H_4O_6$).

*Citric Acid*, $C_6H_8O_7$, occurs abundantly in lemons and oranges, and in small quantities in currants, gooseberries, and raspberries. It is a white crystalline solid, very soluble in water. The taste is sour, but pleasant. The acid and its magnesium salt are used as medicines. The acid itself is used in calico printing. Citric acid is tribasic.

## Esters

Esters are compounds of carbon, hydrogen, and oxygen closely related to alcohols and organic acids. Thus, when ethyl alcohol, acetic acid, and concentrated sulphuric acid are mixed and warmed, **ethyl acetate** is one product. The essential change is represented thus: —

$$\underset{\text{Ethyl Alcohol}}{C_2H_5 . OH} + \underset{\text{Acetic Acid}}{CH_3 . COOH} = \underset{\text{Ethyl Acetate}}{CH_3 . COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

Ethyl acetate has a pleasant, fruitlike odor, and its formation in this way is a simple **test for alcohol or acetic acid.** Ethyl acetate is analogous to sodium acetate, *i.e.* the organic salt contains the radical ethyl, while the metallic salt contains sodium. The fatty acids, as well as those of other series, form many esters of special interest. Some occur naturally

in fruits and flowers, and in many cases give the fragrance and flavor. Others are prepared artificially and used as the characteristic ingredient of cheap flavoring extracts, perfumery, and beverages. Ethyl butyrate has the taste and fragrance of pineapples, amyl acetate of bananas, amyl valerate of apples.

### Fats, Glycerine, and Soap

**General Relations.** — Natural fats and oils are essentially mixtures of stearin, palmitin, and olein. Beef and mutton fat are chiefly stearin, lard is mainly palmitin and olein, while oils such as olive oil are largely olein. Stearin and palmitin are solids at the ordinary temperature, but olein is a liquid. These three compounds — stearin, palmitin, and olein — are esters of their corresponding acids and the alcohol glycerine. They are analogous to ethyl acetate. The radical of glycerine is glyceryl, $C_3H_5$. Stearin is glyceryl stearate, palmitin is glyceryl palmitate, and olein is glyceryl oleate. Natural fats and oils, therefore, are mixtures of these and similar esters. Glycerine is a triacid alcohol containing three hydroxyl (OH) groups. Like ordinary alcohol, it interacts with the fatty acids and forms esters. The latter, as we have just seen, are the fats. Now, when fats are heated with very hot steam or with sulphuric acid, they are changed into glycerine and the corresponding acids. Thus, with stearin the change is —

$$\underset{\text{Stearin}}{(C_{17}H_{35}\,.\,COO)_3C_3H_5} + 3\,H_2O = \underset{\text{Glycerine}}{C_3H_5(OH)_3} + 3\,\underset{\text{Stearic Acid}}{C_{17}H_{35}\,.\,COOH}$$

But if fats are boiled with sodium hydroxide or a similar alkali, glycerine and an alkaline salt of the corresponding acid are formed. **Soap** is a mixture of such alkaline salts. In a few words, the general relations are these: (1) fats are esters; (2) treated with steam or acid, fats form glycerine

and fatty acids; (3) treated with alkalies, fats form glycerine and soap.

**Natural Fats and Oils** are often complex mixtures. The solid fats, as already stated, are rich in stearin and palmitin. **Tallow** is chiefly stearin, but human fat and palm oil are largely palmitin. The soft and liquid fats and oils contain considerable olein, as a rule. The proportion of olein determines the consistency of the fats and oils. Thus, **olive oil** contains 72 per cent of olein (and a similar fat) and about 28 per cent of stearin and palmitin. The specific character of many fats and oils is due mainly to a small proportion of certain fats. These fats correspond to uncommon acids in the fatty, oleic, and other series. **Butter**, for example, consists of the fats corresponding to the following acids: palmitic, stearic, oleic, butyric, capric, and caproic. The last three, together with traces of other substances, give butter its pleasant flavor. Oleomargarine and other substitutes for butter resemble real butter very closely in composition. Artificial butter, however, lacks the flavor of the real butter, but it is "probably just as nutritious, although perhaps not quite so easily digested."

**Glycerine**, $C_3H_8O_3$ or $C_3H_5.(OH)_3$, is a thick, sweet liquid. It mixes readily with water and with alcohol in all proportions, and absorbs moisture from the air. Heated in the air it decomposes and gives off irritating gases, like those produced by burning fat.

Glycerine is used to make nitroglycerine (see below), toilet soaps, and printer's ink rolls; it is also used as a solvent, a lubricator, a preservative for tobacco, and certain foods, a sweetening substance in certain liquors, preserves, and candy; as a cosmetic; and owing to its non-volatile and non-drying properties, it is used as an ingredient of certain inks and oils.

Glycerine is a by-product in the manufacture of soap, or it is made directly by decomposing fats with steam under pressure or with lime. All these methods involve the chemical change described above, viz. the decomposition of an ester (the fat) into the corresponding alcohol (glycerine) and a mixture of fatty acids. By skillful treatment the glycerine is freed from the water and impurities.

As already stated, glycerine is an alcohol, and for this reason it is often called **glycerol**. When treated with a mixture of concentrated nitric and sulphuric acids, it forms an ester commonly known as nitroglycerine ($C_3H_5(ONO_2)_3$). This is a yellow, heavy, oily liquid. It is the well-known explosive, and is also an ingredient of some other explosives. When kindled by a flame, it burns without explosion; but if struck by a hammer or heated suddenly by a percussion cap, it explodes violently. Nitroglycerine is used in blasting; but since it is dangerous to handle and transport, it is usually mixed with some porous substance, such as infusorial earth, fine sand, or even sawdust. In this form it is called **dynamite**.

**Soap**, as already stated, is a mixture of alkaline salts of organic acids, mainly stearic and palmitic acids. Soap is made by boiling fats with sodium hydroxide or potassium hydroxide. This process is called **saponification**. Sodium hydroxide produces hard soap, consisting chiefly of sodium palmitate, sodium stearate, and sodium oleate. Potassium hydroxide produces a soft, semi-fluid soap, which contains mainly the corresponding potassium salts. The chemical change, as already stated, consists in the transformation of an ester (fat) into glycerine and an alkaline salt. In the case of pure stearin (glyceryl stearate) the change may be represented thus: —

$$\underset{\text{Stearin}}{C_3H_5(C_{17}H_{35}\,.\,COO)_3} + 3\,\underset{\substack{\text{Sodium}\\\text{Hydroxide}}}{NaOH} = 3\,\underset{\substack{\text{Sodium}\\\text{Stearate}}}{C_{17}H_{35}COONa} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}$$

The fats used in soap making vary. Tallow, lard, palm oil, and cocoanut oil make white soaps. Bone grease or house grease, together with tallow, palm oil, cottonseed oil, and

rosin, make yellow soaps. Olive oil is used for making castile soap.

In the **cold process** the calculated amounts of alkali and fat are allowed to interact, first in a large tank and then in a box called a "frame." By this process the glycerine and excess of alkali are left in the soap. Most soaps are made by the **boiling process**. The fat and alkali are boiled in a huge kettle. This operation produces a thick, frothy mixture of soap, glycerine, and alkali. At the proper time salt is added, thereby causing the soap to separate and rise to the top. The liquid beneath is drawn off, and from it glycerine is extracted. The soap is often boiled again with rosin or cocoanut oil; then purified by washing, mixed, if desired, with perfume, coloring matter, or some filling material (such as sodium silicate, sand, or borax), cooled in "frames," cut, and dried.

### Carbohydrates

This is a large group, and the most important members are the sugars, starches, and cellulose.

**Sugar.** — The popular term *sugar* means almost any sweet substance found in fruits, nuts, vegetables, sap of trees, etc., though it is usually restricted to the ordinary white sugar obtained from sugar cane and sugar beet. Chemically, there are many sugars, each having a definite constitution. The most important is ordinary sugar, which is also called **cane sugar**, **sucrose**, and **saccharose**. Another important sugar is **glucose**.

**Cane Sugar**, $C_{12}H_{22}O_{11}$, is widely distributed in nature, being found in the sugar cane, sugar beet, sugar maple, Indian corn, sorghum, most sweet fruits, many nuts, blossoms of flowers, and honey. The main source of cane sugar is the sugar cane and sugar beet.

Saccharose, or ordinary sugar, is a white, crystalline solid. Rock candy is highly crystallized sugar. It is soluble in water, but only sparingly soluble in alcohol. If sugar is heated with sulphuric acid, it is changed into a black mass

which is mainly carbon; several gases are also produced, such as steam, carbon dioxide, and sulphur dioxide. Cane sugar does not ferment directly.

The manufacture of cane sugar from sugar cane and sugar beets involves two main operations: (1) the preparation of raw sugar and (2) its purification or refining. (1) In the **preparation of raw sugar from sugar cane** the juice is extracted from the cane by crushing the latter between heavy iron rollers. The liquid is then clarified as soon as possible by boiling it with a little lime, removing the scum, which contains much of the impurity, and finally filtering the liquid through bags or a filter press. The purified juice is next evaporated until the cane sugar begins to crystallize from the cooled liquid. The crystals are then separated from the liquid by whirling in a centrifugal machine. The solid product is called muscovado, raw or brown sugar. The thick liquid is the familiar **molasses**. There are several grades of each product. The **preparation of raw sugar from sugar beets** resembles the method used for sugar cane. The washed beets are reduced to a pulp, or cut into slices, and then treated with water. The sugar dissolves in the water. The solution is clarified, evaporated, and separated by processes much like those applied to cane sugar solutions. The raw sugar can scarcely be distinguished from cane sugar. The molasses is unfit for table use, though considerable sugar is extracted from it by means of strontium hydroxide. (See Strontium Hydroxide.) (2) Raw sugar is usually dark colored, and must be refined before it is suitable for most uses. The **refining of sugar** consists in (*a*) purification, and (*b*) recrystallization. (*a*) The raw sugar is purified by first dissolving it in huge tanks. Air is blown in to agitate the heated solution, blood and other substances are sometimes added to entangle the impurities, and lime is also added to precipitate and gather the impurities into a scum or clot. The colored liquid is next filtered, first through cloth bags and then through animal charcoal, from which it runs as a perfectly clear liquid. (*b*) The filtered sirup is now evaporated in a large vacuum kettle. When a sample shows that the evaporation has reached the proper point, the liquid is run off into tanks to crystallize. The crystals of sugar are separated from the sirup by centrifugal machines. The latter is boiled again or sold as sirup for the table. The crystals are dried in a heated tube called a granulator, so that each grain will be separate. Hence the name *granulated sugar*.

**Glucose** is the name of a sugar and of a commercial mixture of glucose and several related substances. Glucose (dextrose or grape sugar, $C_6H_{12}O_6$) is found in many sweet fruits, especially in grapes. It is often associated with **levulose** (fructose or fruit sugar) — an isomeric compound. The two sugars, for example, are found in honey, and in parts of some plants. Both sugars are formed from cane sugar by boiling it with dilute acid. The chemical change, which is an example of hydrolysis, may be represented thus: —

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Both glucose and fructose ferment directly, forming alcohol and carbon dioxide. (See Alcohol.)

The commercial mixture called "glucose" is prepared on a large scale by boiling starch with dilute acid, usually sulphuric acid. The different varieties of commercial glucose are cheaper than cane sugar, and are used extensively in the manufacture of candy, jelly, table sirups, etc. They are also added to wines and liquors, certain medicines, and many thick liquids in which their presence is harmless. In alkaline solutions, glucose is a strong reducing agent, and is used as such in dyeing with indigo. It also reduces an alkaline mixture of copper sulphate, known as Fehling's solution. When this solution is boiled with glucose, a reddish copper compound (cuprous oxide) is formed. The presence of sugar in solution is often shown in this way.

**Starch** is widely distributed in the vegetable kingdom. It is found in wheat, corn, and all other grains; in potatoes, beans, peas, and similar vegetables; and in large quantities in rice, sago, tapioca, and nuts. Many parts of plants contain starch; for example, the stalk, stem, leaves, root, seed, and fruit. The food value of vegetables depends largely upon the starch they contain.

Starch is a white mass, as usually seen. But under the microscope it is found to consist of oval grains varying some-

what with the source (Fig. 50). Starch is only very slightly soluble in water. But if heated with water, the grains swell and burst, partially dissolve, and form a solution which, when cold, becomes the familiar starch paste. Starch in solution is turned blue by iodine, and its presence in many vegetables

FIG. 50. — Starch grains (magnified) — wheat (left), rice (center), corn (right).

and foods can be readily shown by grinding the substance in a mortar with warm water and adding a drop of dilute iodine solution. The composition of starch corresponds to the formula $(C_6H_{10}O_5)_n$; the subject is still being investigated.

**Bread.** — Wheat flour contains about 70 per cent of starch. The remainder is chiefly water and gluten, though small quantities of mineral matter and fat are present. In making bread, the flour, water, and yeast are thoroughly mixed into dough, which is put in a warm place to rise. Fermentation begins at once. The yeast changes the starch into glucose or a similar fermentable substance which undergoes fermentation, forming alcohol and carbon dioxide. The gases escape in part through the dough, which becomes light and porous. When the dough is baked, the heat kills the yeast plant and fermentation stops; but the alcohol, carbon dioxide, and some water escape and puff up the mass still more. The heat, however, soon hardens the starch, gluten, etc., into a firm but porous loaf.

**Cellulose**, $(C_6H_{10}O_5)_n$, is the basis of the cells of plants. Wood, cotton, linen, and paper are largely cellulose. Pure cellulose is a white substance, insoluble in most liquids, but soluble in a mixture of ammonia and copper oxide. Concentrated sulphuric acid dissolves it slowly; and if the solution is diluted and boiled, the cellulose is changed into a mixture of glucose and dextrin. Sulphuric acid of a special strength, if quickly and properly applied to paper, changes it into a tougher form called parchment paper. The latter is often substituted for animal parchment (*e.g.* sheepskin), and has a variety of uses.

Cellulose has properties resembling those of alcohol. Thus it interacts with acids and forms esters. With nitric acid it forms cellulose nitrates, just as glycerine forms glycerine nitrates (see Nitroglycerine). The cellulose nitrates are the basis of smokeless gunpowders. One of the cellulose nitrates is **gun cotton**. It looks like ordinary cotton, and may be spun, woven, and pressed into cakes. It burns with a large flame, if unconfined; but when ignited by a percussion cap or when burned in a confined space, gun cotton explodes violently. It is used in blasting. A solution of cellulose nitrates in a mixture of alcohol and ether is called **collodion**. When poured or brushed upon a glass plate or the skin, the solvent evaporates, leaving behind a thin film. It is used in preparing certain photographic material and as a coating for wounds. A mixture of camphor and cellulose nitrates is called **celluloid**.

**Paper** is chiefly cellulose. Formerly it was made from various kinds of rags, but most paper, especially that used for newspapers, is made from wood. Considerable writing paper, however, is still made from linen rags.

In making paper from wood, the latter is reduced to a pulp, which is washed, spread on a frame or an endless wire gauze, dried, and pressed. The pulp is prepared by two processes, the mechanical and chemical. Mechanical pulp is made by holding a stick of wood against a revolving stone upon which water constantly falls. Chemical pulp is made by heating chipped wood with sodium hydroxide or with acid calcium sulphite (often called calcium bisulphite). The operation is conducted under pressure in huge tanks called digesters.

Chemical pulp has longer and stronger fibers than mechanical pulp. The two kinds of pulp are often mixed. Most paper is loaded, *i.e.* clay, gypsum, or other mineral matter is mixed with the pulp to give the paper body. Paper used for printing or writing is sized, *i.e.* the surface is coated with gelatine, rosin, or a similar substance to prevent the ink from spreading. Many kinds are also smoothed by passing them between heavy rollers.

## Benzene and its Derivatives

**Introduction.** — Coal tar was described in the preceding chapter as a black complex liquid obtained as a by-product in the manufacture of illuminating gas. It is the chief source of benzene and several other hydrocarbons from which hundreds of derivatives can be prepared.

**Benzene**, $C_6H_6$, is a colorless liquid, lighter than water, and has an odor suggesting coal gas. It burns with a luminous, smoky flame, owing to its richness in carbon. Ordinary illuminating gas owes its luminosity partly to benzene. It dissolves fats, resins, iodine, sulphur, and rubber. Benzene is sometimes called **benzol**. It should not be confused with benzine, which is a mixture of hydrocarbons derived from petroleum. Benzene is chiefly used in preparing its derivatives.

**Nitrobenzene**, $C_6H_5 . NO_2$, is a yellow liquid formed by the interaction of benzene and nitric acid. The equation for the chemical change is: —

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{Nitric}\\\text{Acid}}}{HNO_3} = \underset{\substack{\text{Nitro-}\\\text{benzene}}}{C_6H_5 . NO_2} + \underset{\text{Water}}{H_2O}$$

It is volatile, and the vapor, which is poisonous, has the odor of bitter almonds. It is chiefly used in the manufacture of aniline.

**Aniline**, $C_6H_5 . NH_2$, is an oily liquid, slightly heavier than water. It is prepared on a large scale by reducing nitrobenzene with nascent hydrogen, thus: —

$$\underset{\text{Nitrobenzene}}{C_6H_5 . NO_2} + \underset{\text{Hydrogen}}{6\,H} = \underset{\text{Aniline}}{C_6H_5 . NH_2} + \underset{\text{Water}}{2\,H_2O}$$

From aniline are made many compounds known as **aniline dyes.** Vast dyeing industries have risen since the value of coal tar was discovered (about 1860).

**Phenol**, $C_6H_5 . OH$, is a white crystalline solid. It has a smoky odor, is poisonous, and burns the skin. Coal tar is the source of phenol. A solution of phenol in water, popularly called **carbolic acid**, is used as a disinfectant.

**Naphthalene**, $C_{10}H_8$, is a white, lustrous, crystalline solid obtained from coal tar. It has a penetrating, unpleasant odor, and is used as a substitute for camphor under the name of "moth balls." Large quantities of naphthalene are used in making indigo.

**Anthracene**, $C_{14}H_{10}$, is a white crystalline solid, and is obtained from coal tar. It is one of the most important hydrocarbons, because from it alizarin is made. **Alizarin** is a valuable dyestuff, not only because it produces brilliant colors with different mordants, but also because most of these colors are fast; that is, they do not fade like many aniline colors. The Turkey red, so common on cotton goods, is produced by the aid of alizarin. Alizarin was formerly obtained from madder root, but now vast quantities are manufactured.

### Cyanogen and its Derivatives

**Cyanogen** is a compound of carbon and nitrogen having the composition corresponding to the formula $(CN)_2$. It is a colorless gas, has the odor of peach kernels, is exceedingly poisonous, and burns with a purplish flame. It may be prepared by heating mercuric cyanide ($Hg(CN)_2$).

**Hydrocyanic** or **prussic acid**, HCN, is prepared by heating a cyanide with sulphuric acid, just as hydrochloric acid is obtained from a chloride. The solution smells like peach kernels, and is one of the most deadly of all known poisons. It is a feeble acid and dissociates very slightly indeed into the ions $H^+$ and $CN^-$.

**Potassium cyanide**, KCN, and **sodium cyanide**, NaCN, are white, deliquescent solids. They are deadly poisons.

Large quantities are used in gold and silver plating and in the cyanide process of extracting gold from its ores, as described under that metal. The alkaline reaction exhibited by a solution of potassium cyanide has already been discussed. (See Chapter X, last paragraph.)

**Potassium sulphocyanate** or **thiocyanate**, KCNS, is a white crystalline salt, which produces a deep red solution when added to certain soluble iron compounds, and is therefore used to detect this metal. (See Ferric Compounds.)

### Problems

1. Alcohol is 0.8 as heavy as water. What is the weight of 1200 cc. of alcohol?

2. If 10 gm. of pure alcohol are burned, what weight of each product is formed? (Equation is $C_2H_6O + 3\,O_2 = 2\,CO_2 + 3\,H_2O$.)

3. Calculate the percentage composition of (*a*) alcohol ($C_2H_6O$), (*b*) acetic acid ($C_2H_4O_2$), (*c*) cane sugar ($C_{12}H_{22}O_{11}$), (*d*) acetone ($C_3H_6O$).

4. Calculate the simplest formulas of the substances having the composition: (*a*) carbon = 40, hydrogen = 6.67, oxygen = 53.33; (*b*) carbon = 15.8, hydrogen = 5.26, nitrogen = 36.84, sulphur = 42.1; (*c*) carbon = 54.55, hydrogen = 9.09, oxygen = 36.36.

5. Calculate the per cent of carbon in (*a*) glycerine ($C_3H_8O_3$), (*b*) turpentine ($C_{10}H_{16}$).

# CHAPTER XVIII

## Sulphur and its Compounds

Sulphur has been known for ages. The alchemists regarded it as one of the primary forms of matter. The element and its compounds have always played an important part in the development of many industries.

**Occurrence.** — Sulphur, free and combined, is abundant and widely distributed. Free or native sulphur is found usually in volcanic regions. There are also beds associated with gypsum (calcium sulphate). It is believed that some deposits were formed by the reduction of gypsum by microorganisms.

Several important metallic ores are native sulphides, *e.g.* lead sulphide (PbS), zinc sulphide (ZnS), and those of mercury, antimony, and copper. Iron sulphide ($FeS_2$) is also plentiful. The most abundant sulphates are calcium sulphate ($CaSO_4$), barium sulphate ($BaSO_4$), and magnesium sulphate ($MgSO_4$). Volcanic gases often contain sulphur dioxide ($SO_2$) and hydrogen sulphide ($H_2S$). The latter is also found in the water of sulphur springs. Sulphur is a constituent of certain organic compounds found in onions, horse-radish, mustard, garlic, and eggs; some varieties of petroleum and coal also contain sulphur compounds.

**Source.** — Until recently Sicily furnished most of the sulphur used in the world, but considerable is now produced in Japan, Greece, and the United States (especially in Louisiana). Some of the sulphur of commerce is obtained by

roasting iron pyrites ($FeS_2$) as in the manufacture of sulphuric acid. Small amounts are recovered from the calcium sul-

FIG. 51. — Kiln for extracting sulphur from the crude ore. The calcarone is shown as a vertical section (right) and in operation (left).

phide waste of the Leblanc soda process (see Sodium Carbonate), and from the residues of the iron oxide used to purify illuminating gas.

**Extraction.** — For many years sulphur has been extracted from the impure native sulphur in Sicily by a primitive process. The crude sulphur is brought to the surface by laborers, piled loosely in a heap, and covered with powdered or burnt ore or with earth. The heap is ignited at the bottom, and the heat produced by the combustion of some of the sulphur melts the rest, which runs out at the bottom (Fig. 51). In Louisiana, which now furnishes most of the sulphur used in the United States, the underlying deposits are melted by very hot water and forced to the surface through a small pipe (Fig. 52).

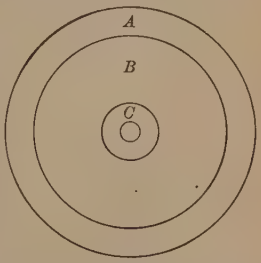



FIG. 52. — Section of a set of pipes for winning sulphur. The water enters through the spaces *A* and *B* and melts the sulphur, which rises part way in *C* and is forced to the surface by compressed air introduced through the innermost pipe.

**Purification.** — Sulphur obtained from its ore usually requires purification, though the Louisiana product is quite pure. This is accomplished by the apparatus shown in Figure 53. The crude sulphur is melted in *B*, and flows into

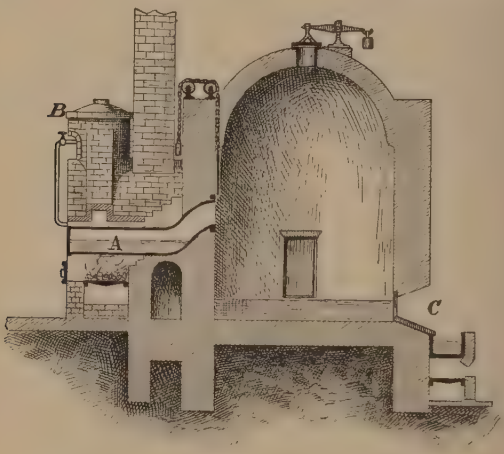



FIG. 53. — Apparatus for purifying sulphur.

the iron cylinder *A*. Here it is heated, and the vapors pass into the large brick chamber, provided with a tap *C*, from which the liquid sulphur may be withdrawn. If the distillation is conducted slowly, the sulphur vapor condenses upon the cold walls of the chamber as a fine powder, called **flowers of sulphur**. As the operation continues the walls become hot, and the sulphur collects on the floor as a liquid which is drawn off into cylindrical wooden molds, forming **roll sulphur** or **brimstone**.

**Properties.** — Ordinary sulphur is a yellow, brittle, crystalline solid. It is practically insoluble in water, but most

varieties dissolve in carbon disulphide, and to some extent in turpentine, chloroform, and benzene ($C_6H_6$). Sulphur does not conduct heat well, the warmth of the hand even causing it to crackle and break from the unequal expansion. The specific gravity of the solid is about two. The density of the vapor varies with the temperature. At the lowest temperature at which sulphur can be vaporized, one molecule contains eight atoms ($S_8$), while at 800° C. and higher it contains two atoms ($S_2$).

Heated to 114.5° C. sulphur melts to a thin amber-colored liquid. As the temperature is raised, the liquid darkens and thickens, until at about 230° C. it is black and too thick to be poured from the vessel. Heated still higher, the color remains black but the mass becomes thin, and finally at about 448° C. the liquid boils and turns into a yellowish brown vapor. When cooled slowly, the sulphur undergoes the same series of changes in the reverse order. Sulphur ignites readily and burns with a pale blue flame, forming sulphur dioxide gas ($SO_2$); if burned in oxygen, a little sulphur trioxide ($SO_3$) is also formed. Finely divided sulphur oxidizes in moist air, forming sulphuric acid ($H_2SO_4$). It also combines directly and readily with hydrogen, carbon, chlorine, and other elements, especially metals; the compounds formed are sulphides. The reaction between sulphur and metals is often attended by vivid combustion, though heat is necessary to start the chemical action. Thus, when a mixture of flowers of sulphur and powdered iron is heated, the mass begins to glow and soon becomes red-hot, the glow often spreading through the mass after removal from the flame. The product is iron sulphide, and the chemical change is represented thus: —

$$\underset{\text{Iron}}{Fe} + \underset{\text{Sulphur}}{S} = \underset{\text{Iron Sulphide}}{FeS}$$

Heated copper glows when dropped into melted sulphur, while zinc dust and flowers of sulphur combine with almost explosive violence.

**Different Forms of Sulphur.** — Sulphur exists in at least three different forms, — two crystallized and one amorphous. These modifications differ in specific gravity, solubility, and other properties. The crystallized forms belong to the orthorhombic and monoclinic systems. (See Appendix, § 3). Orthorhombic sulphur is the form deposited by crystallization from a solution of carbon disulphide. Crystallized native sulphur and ordinary roll sulphur are orthorhombic, though the latter usually consists of such a mass of interlaced crystals that the form is obscured. The monoclinic sulphur is the form deposited as crystals from molten sulphur. By melting sulphur in a crucible and pouring off the excess of liquid as soon as crystals shoot out from the walls near the surface, the interior of the crucible is found to be lined with long, dark yellow, shining needles. They are monoclinic crystals of sulphur. After a few days they gradually become dull, and begin to crumble into minute orthorhombic crystals. This change is mainly due to the fact that monoclinic sulphur cannot exist as such except between 96° C. and 119° C. (its melting point), while orthorhombic sulphur can exist as such only below 96° C. Above 96° C. orthorhombic becomes monoclinic, below 96° C. monoclinic becomes orthorhombic. This temperature at which the two forms of sulphur pass into one another is called the **transition point**. These two varieties of crystallized sulphur have different properties. Thus, orthorhombic sulphur has a specific gravity of 2 and a melting point of 114.5° C., while the corresponding values of monoclinic sulphur are 1.96 and 119° C. Amorphous sulphur is formed by pouring boiling sulphur into cold water. It is a tough, plastic, rubberlike,

amber-colored mass, insoluble in carbon disulphide. It is entirely different in color and texture from the crystallized varieties. It soon becomes hard, brittle, and yellow, and ultimately acquires many properties of ordinary sulphur. Amorphous sulphur is sometimes found in flowers of sulphur and can be detected by its insolubility in carbon disulphide. Other varieties of sulphur also contain amorphous sulphur. One is a white or whitish powder, made by boiling flowers of sulphur with milk of lime and adding hydrochloric acid to the decanted liquid; a fine sulphur powder is precipitated, which gives the liquid the appearance of milk, hence the name often applied to it, "milk of sulphur."

**Uses.** — Sulphur is used in making sulphuric acid and other sulphur compounds, gunpowder, fireworks, matches, in vulcanizing rubber, as a medicine and a constituent of some ointments, and as a germicide for Phylloxera — an insect which destroys grapevines.

**The Important Compounds of Sulphur** are hydrogen sulphide and other sulphides (especially metallic sulphides), sulphur dioxide and trioxide, the sulphites, sulphuric acid and the sulphates, and carbon disulphide.

## Hydrogen Sulphide

**Hydrogen sulphide**, $H_2S$, is a gaseous compound of sulphur and hydrogen, and is sometimes called sulphuretted hydrogen or hydrosulphuric acid. It occurs in some volcanic gases and in the waters of sulphur springs. It is often found in the air, especially near sewers and cesspools, since it is one product of the decay of organic substances containing sulphur. It is one of the impurities of crude illuminating gas.

**Preparation.** — The gas is prepared in the laboratory by the interaction of dilute acids and metallic sulphides; usually dilute hydrochloric acid and ferrous sulphide are used. When the acid is poured upon fragments of the sulphide, the gas is rapidly evolved without applying heat, and may be collected over water. The equation for the chemical change is —

$$\underset{\text{Iron Sulphide}}{FeS} + \underset{\text{Hydrochloric Acid}}{2\,HCl} = \underset{\text{Hydrogen Sulphide}}{H_2S} + \underset{\text{Iron Chloride}}{FeCl_2}$$

**Properties.** — Hydrogen sulphide gas is colorless and has the odor of rotten eggs. It is poisonous. A little, even if diluted with air, often produces headache and nausea, and a large quantity of the gas is fatal. Care should be used in working with hydrogen sulphide, especially if the generator is large. The dry gas is slightly heavier than air; a liter under standard conditions weighs 1.537 gm. It has been liquefied and solidified by the usual methods. Hydrogen sulphide is soluble in water, one volume of water dissolving about three volumes of the gas at the ordinary temperature; the dissolved gas can be completely removed by boiling the solution. The solution is called hydrogen sulphide water, and is often used instead of the gas in chemical experiments. The solution decomposes slowly, sulphur being deposited.

Hydrogen sulphide gas is inflammable and burns with a bluish flame, forming water and sulphur dioxide, thus: —

$$\underset{\text{Hydrogen Sulphide}}{2\,H_2S} + \underset{\text{Oxygen}}{3\,O_2} = \underset{\text{Sulphur Dioxide}}{2\,SO_2} + \underset{\text{Water}}{2\,H_2O}$$

If the supply of air is insufficient, combustion is incomplete, water and sulphur being formed, thus: —

$$\underset{\text{Hydrogen Sulphide}}{2\,H_2S} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Water}}{2\,H_2O} + \underset{\text{Sulphur}}{2\,S}$$

It is a reducing agent, and is used as such in chemical experiments. Even sulphuric acid is reduced by it, thus: —

$$\underset{\text{Sulphuric Acid}}{H_2SO_4} + \underset{\text{Hydrogen Sulphide}}{H_2S} = \underset{\text{Sulphur Dioxide}}{SO_2} + \underset{\text{Sulphur}}{S} + \underset{\text{Water}}{2\,H_2O}$$

Hydrogen sulphide gas dissolved in water gives a solution which has a feeble acid reaction, is neutralized by bases, and forms salts called sulphides. It dissociates only slightly, the ions being chiefly $H^+$ and $HS^-$.

**Composition of Hydrogen Sulphide Gas.** — When metals are heated in dry hydrogen sulphide, metallic sulphides are formed; and the volume of hydrogen liberated by their decomposition is the same as the original volume of gas used. Since the hydrogen molecule contains two atoms ($H_2$), there must be two atoms of hydrogen in the hydrogen sulphide molecule. The vapor density of hydrogen sulphide gas as found by experiment requires the molecular weight 34 (approximately). Subtracting 2 for 2 H, the remainder (32) agrees well with the atomic weight of sulphur. Hence, there can be only one atom of sulphur in hydrogen sulphide, and the formula must be $H_2S$.

**Sulphides** may be regarded as salts of the weak acid, hydrosulphuric acid, though they are not always prepared directly from hydrogen sulphide by the substitution of a metal for its hydrogen. They may be produced by the direct union of sulphur and metals (as in the case of iron and copper sulphides previously mentioned), by exposing the metal to the moist gas, or by the reduction of a sulphate with carbon. A more common way is to precipitate them by passing the gas into solutions of metallic compounds, or sometimes, by adding hydrogen sulphide water to such solutions. Copper, tin, lead, and silver are rapidly tarnished by the gas. Silverware, on this account, turns brown or black, especially in houses heated by coal or lighted by coal gas. The brown silver sulphide also coats silver spoons

which are put into mustard or eggs. Lead compounds are blackened by this gas, owing to the formation of lead sulphide, thus: —

$$\underset{\text{Lead Oxide}}{PbO} + \underset{\text{Hydrogen Sulphide}}{H_2S} = \underset{\text{Lead Sulphide}}{PbS} + \underset{\text{Water}}{H_2O}$$

For this reason houses painted with "white lead" paint often become dark, and, similarly, oil paintings are discolored. The darkening (to brown or black) of the solution of a lead compound is the customary **test for hydrogen sulphide.**

Many sulphides have a brilliant color. Arsenious sulphide is pale yellow, cadmium sulphide is golden yellow, manganese sulphide is flesh colored, zinc sulphide is white, antimony sulphide is orange red. They vary in solubility. Most sulphides are insoluble in water. The sulphides of lead, silver, copper, and some other metals are insoluble in dilute hydrochloric acid. The sulphides of iron, zinc, and some other metals are decomposed by dilute hydrochloric acid, but are precipitated if ammonium hydroxide is present. Sulphides of certain metals dissolve in water. Hence by precipitating metals under different conditions, groups of metals may be separated and subjected to further tests. The color often affords a ready means of detecting each sulphide. Hydrogen sulphide is thus a serviceable reagent in Qualitative Analysis.

## Oxides of Sulphur

**Sulphur Dioxide,** $SO_2$, is the common compound of sulphur and oxygen. It occurs in the gases of volcanoes, and to a slight extent in the atmosphere, since it is the usual product of the combustion of sulphur and sulphur compounds.

**Preparation.** — When sulphur burns in air (or oxygen), sulphur dioxide is formed, thus: —

$$\underset{\text{Sulphur}}{S} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Sulphur Dioxide}}{SO_2}$$

It is also formed by roasting iron disulphide (iron pyrites) in the air, thus: —

$$\underset{\text{Iron Disulphide}}{2\,FeS_2} + \underset{\text{Oxygen}}{11\,O} = \underset{\text{Sulphur Dioxide}}{4\,SO_2} + \underset{\text{Iron Oxide}}{Fe_2O_3}$$

The foregoing reaction is utilized on a large scale in the commercial manufacture of sulphuric acid. Sulphur and carbon reduce sulphuric acid to sulphur dioxide, thus: —

$$\underset{\text{Sulphur}}{S} + \underset{\text{Sulphuric Acid}}{2\,H_2SO_4} = \underset{\text{Sulphur Dioxide}}{3\,SO_2} + 2\,H_2O$$

$$\underset{\text{Carbon}}{C} + 2\,H_2SO_4 = 2\,SO_2 + \underset{\text{Carbon Dioxide}}{CO_2} + 2\,H_2O$$

Two methods of preparation are used in the laboratory. (1) If copper and concentrated sulphuric acid are heated, a series of complex changes results finally in the evolution of sulphur dioxide. The equation is usually written: —

$$\underset{\text{Copper}}{Cu} + \underset{\text{Sulphuric Acid}}{2\,H_2SO_4} = \underset{\text{Sulphur Dioxide}}{SO_2} + \underset{\text{Copper Sulphate}}{CuSO_4} + 2\,H_2O$$

(2) Sulphuric (or hydrochloric) acid dropped upon a sulphite yields sulphur dioxide, thus: —

$$\underset{\text{Sodium Sulphite}}{Na_2SO_3} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Sulphur Dioxide}}{SO_2} + \underset{\text{Sodium Sulphate}}{Na_2SO_4} + H_2O$$

The latter method is convenient for liberating a steady current of the gas.

**Properties.** — Sulphur dioxide gas has no color. It has a suffocating odor, being the well-known odor associated with burning sulphur matches. It will not burn in the air, nor will it support ordinary combustion. A burning taper or stick of wood is instantly extinguished by it, but finely

divided metals, iron for example, burn in it. It is a heavy gas, the high density (2.2) allowing it to be readily collected by displacement of air, as in the case of chlorine. A liter of sulphur dioxide under standard conditions weighs 2.927 gm. Its critical temperature is about + 155.5° C., and at a moderately low temperature it changes into a transparent, colorless liquid, which boils at − 8° C.; if sufficiently cooled, it freezes into a transparent, icelike solid, which melts at about − 76° C. Liquid sulphur dioxide is a common commercial article. Sulphur dioxide gas is very soluble in water. At the ordinary temperature one volume of water dissolves about forty volumes of gas, but the solution loses it all by boiling. This solution is sour and reddens blue litmus, and contains **sulphurous acid** (see below). Moist sulphur dioxide bleaches vegetable coloring matters. A red or purple flower loses color in it. Silk, hair, straw, wool, and other delicate substances, which would be injured by chlorine, are whitened by sulphur dioxide. In some cases the color returns when the bleached article is exposed to the air for some time, and usually such bleached objects become yellow with age. The coloring matter is not wholly destroyed, but probably unites with the sulphur dioxide to form a colorless compound, which slowly decomposes.

**Uses.** — Immense quantities of sulphur dioxide are used in the manufacture of sulphuric acid. The gas is also used to preserve meat and wines, to fumigate clothing and houses, in paper making, in tanning, in refining sugar, and in making acid sodium sulphite. Liquid sulphur dioxide is used in extracting glue and gelatine, and in various metallurgical processes. It absorbs considerable heat during evaporation, and was formerly used in some ice machines.

**The Composition of Sulphur Dioxide** is based on the following: The gas formed by burning sulphur in a measured volume of oxygen

has the same volume as the oxygen itself. Hence there are as many molecules of sulphur dioxide as there were of oxygen; that is, one molecule of sulphur dioxide contains two atoms of oxygen. Two atoms of oxygen weigh 32. But the molecular weight of sulphur dioxide calculated from an experimental determination of its vapor density is about 64. Subtracting 32 (*i.e.* $2 \times 16$) for the oxygen (2 O) from this, there remains about 32 for sulphur. The atomic weight of sulphur is 32.07; hence sulphur dioxide contains only one atom of sulphur, and its composition is expressed by the formula $SO_2$.

**Sulphur Trioxide**, $SO_3$, is formed by the direct union of sulphur dioxide and oxygen, though a little is produced when sulphur burns in air or in oxygen. The action is slow, but can be hastened by passing a mixture of sulphur dioxide and oxygen (or air) over hot platinum, or better over asbestos coated with platinum. Other substances also hasten the chemical change. At the ordinary temperature sulphur trioxide is a liquid, which boils at 46° C. and solidifies at 15° C. to a white crystalline mass. Another solid form, silklike in luster and appearance, is known. When exposed to moist air, it fumes strongly, forming sulphuric acid; and when dropped into water, it dissolves with a hissing sound and evolution of heat. The equation for this chemical change is —

$$\underset{\text{Sulphur Trioxide}}{SO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric Acid}}{H_2SO_4}$$

## Oxygen Acids and Salts of Sulphur

**Sulphurous Acid and Sulphites.** — Sulphurous acid, $H_2SO_3$, is formed when sulphur dioxide dissolves in water. Sulphur dioxide is, therefore, sulphurous anhydride. The simplest equation expressing this fact is —

$$\underset{\text{Sulphur Dioxide}}{SO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphurous Acid}}{H_2SO_3}$$

This acid is known only in solution, and resembles carbonic acid in this respect. It is unstable and decomposes readily into sulphur dioxide and water. It gradually forms sulphuric acid by combining with oxygen from the air and very rapidly by interaction with oxidizing agents, such as potassium permanganate. Sulphurous acid is dibasic, and forms two classes of salts, the normal and acid sulphites. They are reducing agents, and yield sulphur dioxide when treated with acids. It will be recalled in this connection that a convenient method of preparing sulphur dioxide is the decomposition of normal sodium sulphite ($Na_2SO_3$) by sulphuric or hydrochloric acid. The sulphite first forms sulphurous acid ($H_2SO_3$), and the unstable acid decomposes into water and sulphur dioxide. The following equations express these two reactions: —

$$\underset{\text{Sodium Sulphite}}{Na_2SO_3} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Sulphurous Acid}}{H_2SO_3} + \underset{\text{Sodium Sulphate}}{Na_2SO_4}$$

$$\underset{\text{Sulphurous Acid}}{H_2SO_3} = \underset{\text{Sulphur Dioxide}}{SO_2} + \underset{\text{Water}}{H_2O}$$

**Acid sodium sulphite** ($HNaSO_3$), often called bisulphite of soda, is the anticolor used to remove the excess of chlorine from bleached cotton cloth. It is also used in brewing, tanning, and in the manufacture of starch, sugar, and paper. Acid calcium sulphite ($CaH_2(SO_3)_2$), also called bisulphite of calcium, is prepared by passing sulphur dioxide into milk of lime, and is used in paper making.

Sulphurous acid is rather weak. In terms of the theory of electrolytic dissociation it dissociates only to a comparatively slight extent, the ions being chiefly $H^+$ and $HSO_3^-$; the latter ion, however, dissociates to some degree into $H^+$ and $SO_3^{--}$. Solutions of the acid sulphites of sodium and potassium have an acid reaction owing to the slight disso-

ciation of the $HSO_3$-ion into the ions $H^+$ and $SO_3^{--}$. Solutions of the normal sulphites of sodium and potassium are alkaline. This fact is briefly explained in terms of the theory of electrolytic dissociation as follows: The $SO_3$-ions from the sulphite tend to form the more stable $HSO_3$-ions by combining with the H-ions furnished by the appreciably dissociated water; hence OH-ions are left in the solution and give it an alkaline reaction. As already stated, cases of double decomposition like the one just cited in which water is one factor are illustrations of hydrolysis (see Hydrolysis, Chapter X).

**Sulphuric Acid**, $H_2SO_4$, is found in the waters of a few rivers and mineral springs. It is manufactured in enormous quantities and used for many purposes.

Sulphuric acid was doubtless known to the Arabian alchemists living in the tenth century. It was definitely mentioned by Basil Valentine in the fifteenth century, who described its preparation by heating a mixture of iron sulphate (green vitriol) and sand. The product, an oily liquid, was called oil of vitriol, a name now often used. About 1740, the method of burning sulphur and oxidizing the product was introduced into England.

**The Manufacture of Sulphuric Acid**, as usually conducted, is based upon the fact that the oxidation of sulphur dioxide in the presence of water forms sulphuric acid. The apparent equation for the chemical change is: —

$$\underset{\text{Sulphur Dioxide}}{SO_2} + O + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric Acid}}{H_2SO_4}$$

The oxidation is accomplished in two ways. In the older process, known as the chamber process, oxides of nitrogen are used. In the newer process, called the contact process, the oxidation is brought about by oxygen in the presence of a suitable catalytic agent.

In the **chamber process** the general operation consists in passing sulphur dioxide, air, steam, and oxides of nitrogen into large lead chambers. These gases interact and ultimately produce sulphuric acid, which collects on the walls and floors of the lead chambers. The oxides of nitrogen lose part of their oxygen by this change and are themselves reoxidized by the oxygen of the air into higher oxides, and become fitted to oxidize more sulphur dioxide. The oxides of nitrogen act as carriers of oxygen, continuously giving oxygen to sulphur dioxide and taking it from the air. Theoretically, a small quantity of the oxides of nitrogen will change an infinite quantity of sulphur dioxide into sulphuric acid, but in actual practice losses occur and oxides of nitrogen must be supplied.

Careful study shows that the chemical changes involved in this process of manufacturing sulphuric acid are complex and variable. According to a reliable authority, the main reactions may be represented thus: —

$$2\,SO_2 + N_2O_3 + O_2 + H_2O = \underset{\text{Nitrosyl-sulphuric Acid}}{2\,SO_2(OH)(ONO)}$$

$$2\,SO_2(OH)(ONO) + H_2O = 2\,H_2SO_4 + N_2O_3$$

The nitrogen trioxide ($N_2O_3$) is apparently an essential factor, though according to some authorities the change may be due to a mixture of nitric oxide (NO) and nitrogen peroxide ($NO_2$). Under some conditions, nitric oxide plays a prominent part. It may be said in general that the ease with which the oxides of nitrogen pass into each other makes it highly probable that they are carriers of oxygen from the air to the sulphur dioxide.

The details of a **sulphuric acid plant**, together with the courses taken by the gases, are shown in Figure 54. There are three main parts: (*a*) the furnace for producing sulphur dioxide, (*b*) the lead

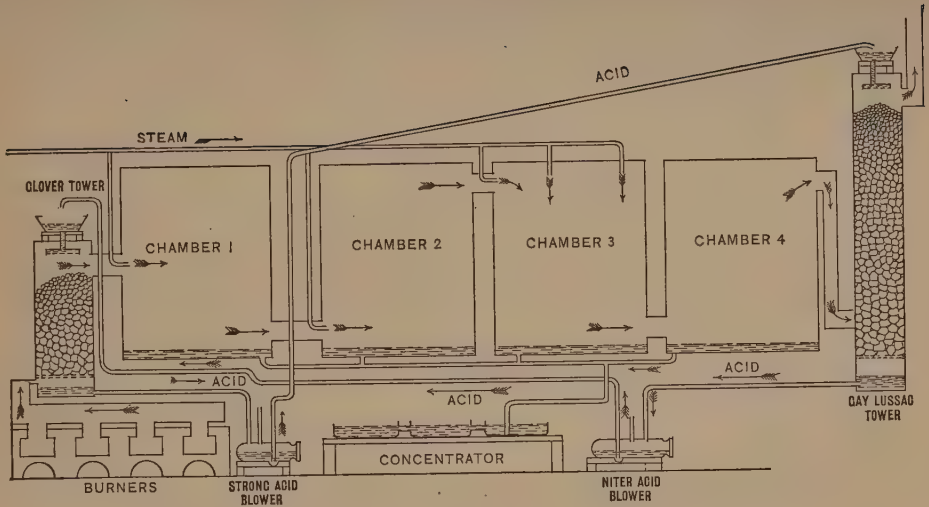



FIG. 54. — Apparatus for manufacturing sulphuric acid by the chamber process.

chambers together with the Glover and Gay-Lussac towers for changing the sulphur dioxide into sulphuric acid, and (*c*) the concentrating apparatus. The manufacture is conducted as follows: (1) Sulphur or iron disulphide (iron pyrites, $FeS_2$) is burned in a furnace so constructed that enough air passes over the burning mass to change the sulphur into sulphur dioxide, and to furnish the proper amount of oxygen for later changes. In some works the furnace is provided with "niter pots" containing a mixture of sodium nitrate and sulphuric acid; the nitric acid vapors which are formed in these vessels are one source of the oxides of nitrogen. (2) The mixture of sulphur dioxide, oxides of nitrogen, and air passes from the furnace into the bottom of the Glover tower. This is a tall tower filled with small stones over which flow two streams of sulphuric acid, one dilute and the other containing oxides of nitrogen (obtained from the Gay-Lussac tower). These acids not only cool the ascending gases, but are themselves deprived of water and oxides of nitrogen. Hence, concentrated acid flows out of the bottom of the Glover tower, while from the top sulphur dioxide, oxides of nitrogen, steam, and air pass on into the first lead chamber. Here nitric acid is often introduced, as well as steam. The main chemical changes occur in this and in the second chamber. A third chamber serves mainly to cool and dry the gases. These chambers are huge boxes often having a total capacity of 150,000 cubic feet; the walls and floors are of sheet lead supported on a wooden framework, lead being a metal which is only slightly attacked by the chamber acid. The remaining gases pass on into the bottom of the Gay-Lussac tower. This tower is filled with coke or perforated balls over which flows concentrated sulphuric acid (from the Glover tower), which absorbs the unused oxides of nitrogen. These oxides, as stated above, are liberated again in the Glover tower, hence there is little loss. At the end of the plant is a tall chimney, which serves as an exit for unused gases (such as nitrogen) and also creates a draft strong enough to carry the gases through the chambers and tower. (3) The acid which is produced in the chambers and drawn off from them at intervals contains from 60 to 70 per cent of the compound $H_2SO_4$. Ordinary commercial sulphuric acid, which contains about 96 to 98 per cent, is prepared from the chamber acid by evaporation, first in lead pans and finally in a platinum vessel.

In the **contact process** sulphur dioxide and air, carefully purified and cooled to the proper temperature (350°–400° C.),

are led through pipes containing a contact mixture, which is chiefly finely divided platinum. The sulphur dioxide is oxidized to sulphur trioxide, thus: —

$$2\ SO_2 + O_2 = 2\ SO_3$$

The sulphur trioxide is conducted into sulphuric acid or water, thus producing a pure acid of any desired strength. In the contact process the platinum is apparently not changed, nor does it cause the sulphur dioxide to unite with the oxygen. It hastens the rather slow chemical action between the gases, somewhat as oil assists the movement of machinery. This hastening of chemical action, as we have already learned, is called **catalysis** or **catalytic action.** The substance which hastens a chemical reaction, but appears unchanged at the end of the process, is called a catalyzer.

**Properties of Sulphuric Acid.** — Sulphuric acid is an oily liquid, colorless when pure, but usually brown from the presence of charred organic matter, such as dust and straw. The specific gravity of the commercial acid is about 1.83. When sulphuric acid is mixed with water, much heat is evolved. The acid should always be poured into the water, otherwise the intense heat may crack the vessel or spatter the hot acid. The volume of dilute acid produced is smaller than the sum of the volumes of water and concentrated acid. The tendency to absorb water is shown in many ways. The concentrated acid absorbs moisture from the air and from gases passed through it. It is often used in the laboratory to dry gases, since it is not volatile at the ordinary temperature. Wood, paper, sugar, starch, cotton cloth, and many organic substances are blackened by sulphuric acid. Such compounds contain hydrogen and oxygen in the proportion to form water; these two elements are abstracted and carbon alone remains. Similarly, sul-

phuric acid withdraws water from the flesh, making painful wounds.

Sulphuric acid boils at about 330° C., but begins to give off fumes of sulphur trioxide at about 150° C. It oxidizes carbon and sulphur to carbon dioxide and sulphur dioxide, owing to its instability when heated with these elements. Metals decompose it, yielding various products, such as hydrogen, sulphur dioxide, or hydrogen sulphide. It combines directly with ammonia gas, thus: —

$$\underset{\text{Ammonia Gas}}{2\,NH_3} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Ammonium Sulphate}}{(NH_4)_2SO_4}$$

Its interaction with salts, such as chlorides, nitrates, and sulphites, which results in the liberation of the corresponding acid, has already been discussed. A solution of sulphuric acid in water contains hydrogen ions ($H^+$), monovalent ions ($HSO_4^-$), and divalent ions ($SO_4^{--}$), depending upon the concentration. Dilute solutions contain an abundance of $SO_4$-ions ($SO_4^{--}$).

**Uses of Sulphuric Acid.** — Sulphuric acid is one of the most important substances. Directly or indirectly it is used in hundreds of industries upon which the comfort, prosperity, and progress of mankind depend. It is used in the manufacture of other mineral acids and many organic acids. It is essential in one process of manufacturing sodium carbonate. Enormous quantities are consumed in making artificial fertilizers, alum, nitroglycerine, glucose, phosphorus, dyestuffs, and in various parts of such fundamental industries as dyeing, bleaching, electroplating, refining, and metallurgy.

**Sulphates.** — Sulphuric acid is dibasic and forms two classes of salts, — the **normal sulphates**, such as $Na_2SO_4$,

and the **acid sulphates**, such as $HNaSO_4$. The normal sulphates are rather stable salts; many yield sulphur trioxide when heated to a high temperature. The acid salts lose water when heated, yielding in addition salts called pyrosulphates (see below under pyrosulphuric acid). Most sulphates are soluble in water, only the sulphates of barium, strontium, and lead being insoluble, while calcium sulphate is slightly soluble. Important sulphates are calcium sulphate (gypsum, $CaSO_4 . 2H_2O$), barium sulphate (heavy spar, $BaSO_4$), zinc sulphate (white vitriol, $ZnSO_4$), copper sulphate (blue vitriol or bluestone, $CuSO_4$), iron sulphate (green vitriol, copperas, ferrous sulphate, $FeSO_4$), sodium sulphate (Glauber's salt, $Na_2SO_4$), and magnesium sulphate (Epsom salts, $MgSO_4$, and kieserite, $MgSO_4 . H_2O$). Sulphates are widely used as medicine and in many industries. They are described more fully under the individual metals.

The **test for sulphuric acid or a soluble sulphate** is the formation of white, insoluble barium sulphate upon the addition of barium chloride solution. An insoluble sulphate, such as calcium sulphate, when fused on charcoal is reduced to a sulphide, which blackens a moist silver coin. The blackening is due to the formation of silver sulphide.

The usual test, as already stated, is applicable to both the acid and soluble sulphates because their solutions contain $SO_4$-ions. When a solution containing barium ions is added, the ions $Ba^{++}$ and $SO_4^{--}$ unite and form barium sulphate, which is insoluble in water and is not (like some other barium salts) decomposed by the common acids. The ionic equation for the reaction is :—

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4$$

**Fuming Sulphuric Acid**, $H_2S_2O_7$, is made by adding sulphur trioxide to sulphuric acid, or by heating moist ferrous sulphate. It is sometimes called Nordhausen sulphuric

acid. It is a thick, brown liquid, which fumes strongly in the air, owing to the escape of oxides of sulphur. It is used in gas analysis to absorb ethylene and other illuminants, and in dyeing to dissolve indigo. If the fuming acid is cooled to 0° C., crystals separate; they are called pyrosulphuric acid or disulphuric acid. Its salts are the pyrosulphates.

### Other Sulphur Compounds

**Sodium Thiosulphate**, $Na_2S_2O_3$, is a salt of an unstable acid. It is sometimes incorrectly called sodium hyposulphite, or simply "hypo." It is a white, crystalline solid, very soluble in water. The solution, used in excess, dissolves the halogen compounds of silver, *i.e.* AgCl, AgBr, AgI; hence its extensive use in photography. (See Photography.) It is used in dyeing, and in chemical analysis (for determining the amount of free iodine in a solution).

**Carbon Disulphide** (or Carbon Bisulphide, $CS_2$) when pure is a clear, colorless liquid, with an agreeable odor; the commercial substance is yellow and has an offensive odor. It is poisonous. Carbon disulphide is an endothermic compound, *i.e.* its synthesis from its elements is accompanied by absorption of heat. The thermal equation for the formation of carbon disulphide is —

$$\underset{\text{Carbon}}{C} + \underset{\text{Sulphur}}{S_2} = \underset{\substack{\text{Carbon}\\\text{Disulphide}}}{CS_2} - 28{,}700 \text{ cal.}$$

Like all endothermic compounds it is relatively unstable and can be exploded by fulminating mercury. Ordinarily it can be handled without danger of explosion. It is volatile and extremely inflammable, the equation for its combustion being —

$$\underset{\substack{\text{Carbon}\\\text{Disulphide}}}{CS_2} + \underset{\text{Oxygen}}{3\,O_2} = \underset{\substack{\text{Carbon}\\\text{Dioxide}}}{CO_2} + \underset{\substack{\text{Sulphur}\\\text{Dioxide}}}{2\,SO_2}$$

This liquid is practically insoluble in water. It dissolves rubber, gums, fats, resins, iodine, camphor, and some forms of sulphur. It is a highly refracting liquid, and hollow glass prisms filled with it are used to decompose light. As a solvent it is used to dissolve pure rubber in the manufacture of rubber cement. It is also used to kill insects on both living and dried plants (*e.g.* in museums), and to exterminate burrowing animals, such as moles and woodchucks. Many oils, waxes, and greases are extracted by carbon disulphide.

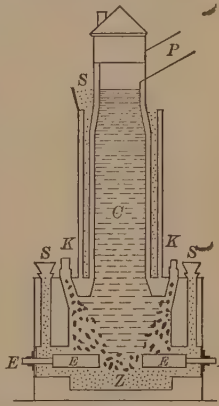


FIG. 55. — Furnace for the manufacture of carbon disulphide.

Until recently carbon disulphide was manufactured by passing sulphur vapor over red-hot coke or charcoal in iron or earthenware retorts. The product required laborious purification. It is now manufactured by an electrothermal process in a furnace somewhat like that shown in Fig. 55. Several groups of carbon electrodes (*E*, *E*) are set into the base of a furnace, coke is packed loosely between them; sulphur is put into *Z* and partly surrounds the electrodes. The body of the furnace is filled with charcoal (*C*). Sulphur is introduced at suitable points (*S*, *S*, *S*), and coke is fed in through *K*, *K*. When the current passes, the sulphur melts and unites with the heated carbon above the electrodes. The vapors of the resulting carbon disulphide escape from the top of the furnace through *P*, and are condensed in a special apparatus.

## Problems

1. Calculate the percentage composition of (*a*) barium sulphate ($BaSO_4$), (*b*) zinc sulphate ($ZnSO_4$), (*c*) sodium sulphate ($Na_2SO_4$).

2. Calculate the percentage composition of (*a*) galena (PbS), (*b*) zinc blende (ZnS), (*c*) iron pyrites ($FeS_2$), (*d*) ferrous sulphide (FeS).

3. What weight and what volume of hydrogen can be obtained from 102 gm. of hydrogen sulphide?

4. What is the weight of a stick of brimstone 10 cm. long and 4 cm. in diameter?

5. How many grams of ferrous sulphide are needed to prepare a liter of hydrogen sulphide gas?

6. (*a*) Sulphuric acid is 1.84 times heavier than water. How many grams of acid will a liter flask hold? (*b*) What weight of acid is needed to fill a carboy holding 5 gallons?

7. Calculate the weight of oxygen necessary to burn (to sulphur dioxide) 731 gm. of sulphur containing 15 per cent of impurities.

8. A lump of sulphur weighing 32 gm. is burned in air. Calculate (*a*) the weight of oxygen required, and (*b*) the weight of sulphur dioxide formed.

9. How many liters of oxygen are needed (*a*) to form 10 l. of sulphur dioxide by burning sulphur in air, and (*b*) to change 10 l. of sulphur dioxide to sulphur trioxide?

10. Suppose 10 gm. of lead yield 14.642 gm. of lead sulphate ($PbSO_4$). Calculate the atomic weight of sulphur on the assumption that the atomic weights of lead and oxygen are 206.91 and 16 respectively.

11. Suppose 112.1943 gm. of silver yield 128.8288 gm. of silver sulphide ($Ag_2S$). What is the atomic weight of sulphur, if the atomic weight of silver is accepted as 107.88?

12. Write the formulas of the following compounds by applying the principle of valence discussed in Chapter XIV: Potassium sulphite, acid potassium sulphite, calcium sulphate, acid calcium sulphite, ammonium sulphide, ammonium sulphate, calcium sulphide.

13. A graduated cylinder is filled to the 250 cc. mark. A lump of sulphur weighing 90 gm. is dropped in, and the water rises to the 295 cc. mark. Calculate the specific gravity of sulphur.

14. Sulphur and oxygen combine in the ratios (*a*) 1 : 1 and (*b*) 2 : 3. Write the simplest chemical equations corresponding to these reactions.

15. Write the ionic equation for the transformation of sodium sulphate into barium sulphate by barium chloride.

# CHAPTER XIX

## Classification of the Elements

**Introduction.** — In the preceding chapters emphasis has been laid on the individual elements, especially oxygen, hydrogen, nitrogen, carbon, chlorine, and sulphur. These elements differ from each other in many ways, and if this diversity prevailed among all the eighty elements, it would be difficult to proceed very far with the study of chemistry. Fortunately the elements are not independent. Certain ones are so similar in their chemical relations that they can be put into the same class. Several characteristic classes have been formed. The arrangement into groups or classes not only simplifies the study of the elements, but reveals many fundamental relations.

**Classification of the Elements.** — Many attempts have been made to classify the elements. About the time of Lavoisier (1743–1794) they were roughly divided into **metals and non-metals**. Those elements were called metals which were hard, lustrous, heavy, and good conductors of heat, while the others were called non-metals. This classification proved to be misleading as additional elements were discovered whose properties did not harmonize with the principle of division. It is used at the present time, however, because many common elements fall readily into one of these classes, as shown in the lists of metals and non-metals given in Chapter X.

Classification according to **acid and basic properties** prevailed for a time. But it was abandoned largely because such a basis of division excluded elements exhibiting both

acid and basic properties, such as zinc and chromium. The elements have also been classified according to their **valence** into six or seven groups (the mono-, di-, tri-, etc.). But this plan was given up partly because of so many cases of variable valence, but mainly on account of the indiscriminate character of the groups. For example, elements so unlike as sodium and chlorine were in the same group.

About 1828 striking resemblances between certain elements were pointed out, and several **groups or families** were suggested. For example: —

| | | | |
|---|---|---|---|
| Lithium | Selenium | Calcium | Nitrogen |
| Sodium | Sulphur | Strontium | Phosphorus |
| Potassium | Oxygen | Barium | Arsenic |

This classification was arbitrarily based on selected physical and chemical properties. It was interesting but incomplete, because it emphasized resemblances and overlooked differences; that is, the basis of comparison was not broad enough.

The first actual progress began to be made about 1850, when chemists became deeply interested in the significance of atomic weights. Dumas and others pointed out certain striking **numerical relations** between the atomic weights of related elements. Thus, the atomic weight of sodium is half the sum of the atomic weights of lithium and potassium.

$$\text{Li} = 7,\ \text{Na} = 23,\ \text{K} = 39.\quad \frac{7 + 39}{2} = 23$$

The same is true of phosphorus, arsenic, and antimony.

$$\text{P} = 31,\ \text{As} = 75,\ \text{Sb} = 120.\quad \frac{31 + 120}{2} = 75.5$$

A number of such families was found, but this method of classification was not comprehensive, nor did it entirely eliminate chance selections.

The existence of other relations similar to those just

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cited, a deep desire to obtain more accurate atomic weights, and a growing interest in the properties of the elements themselves focused the attention of chemists about 1860 upon the **relation of properties to atomic weights.** Several conditions fostered this principle of classification. One was the atomic weight determinations of Stas, whose masterly work yielded very exact atomic weights. Another was the acceptance by most chemists of a uniform table of atomic weights. A third was the vast accumulation of facts about the elements and their compounds. Chemists were ready for a new and broader classification of the elements.

**The Periodic Classification of the Elements.** — Previous to 1869 no classification included all the elements. In that year the Russian chemist Mendelejeff published an arrangement known as the **periodic classification of the elements.** This classification revealed a new relation between the properties of the elements and their atomic weights, and is very helpful in studying the chemical elements. Mendelejeff's scheme, slightly modified to conform to subsequent discoveries, is substantially as follows: —

If all the elements are arranged in the order of their increasing atomic weights, a series results in which similar or closely related elements occur at regular intervals. That is, the series breaks up into several periods, and hence the system of classification is called periodic. If the series is divided into these periods and the periods placed below each other, a table is secured in which the perpendicular columns consist of groups of similar elements, *i.e.* elements which have similar relations and form analogous compounds which have similar properties. Such a table is shown on the following page. In each group the elements have been subdivided into families in order to emphasize the mutual relationship among closely allied elements.

## Periodic Classification of the Elements

| Periods | Group 0 | Group I | Group II | Group III | Group IV | Group V | Group VI | Group VII | Group VIII |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | H = 1.008 | | | | | | | |
| 2 | He = 4 | Li = 7.00 | Be = 9.1 | B = 11.0 | C = 12.0 | N = 14.01 | O = 16.00 | F = 19.0 | |
| 3 | Ne = 20.0 | Na = 23.00 | Mg = 24.32 | Al = 27.1 | Si = 28.3 | P = 31.0 | S = 32.07 | Cl = 35.46 | |
| 4 | A = 39.9 | K = 39.10 | Ca = 40.09 | Sc = 44.1 | Ti = 48.1 | V = 51.2 | Cr = 52.1 | Mn = 54.93 | Fe = 55.85<br>Ni = 58.68<br>Co = 58.97 |
| 5 | | Cu = 63.57 | Zn = 65.37 | Ga = 69.9 | Ge = 72.5 | As = 75.0 | Se = 79.2 | Br = 79.92 | |
| 6 | Kr = 81.8 | Rb = 85.45 | Sr = 87.62 | Y = 89.0 | Zr = 90.6 | Cb = 93.5 | Mo = 96.0 | | Ru = 101.7<br>Rh = 102.9<br>Pd = 106.7 |
| 7 | | Ag = 107.88 | Cd = 112.40 | In = 114.8 | Sn = 119.0 | Sb = 120.2 | Te = 127.5 | I = 126.92 | |
| 8 | Xe = 128.0 | Cs = 132.81 | Ba = 137.37 | La = 139.0 | Ce – Yb[1]<br>140 – 178 | Ta = 181.0 | W = 184.0 | | Os = 190.9<br>Ir = 193.1<br>Pt = 195.0 |
| 9 | | Au = 197.2 | Hg = 200.0 | Tl = 204.0 | Pb = 207.10 | Bi = 208.0 | | | |
| 10 | | | Ra = 226.4 | | Th = 232.42 | | U = 238.5 | | |

[1] This set includes several elements more or less doubtful or still under investigation.

From the table it is seen that the elements fall naturally into two large general classes called groups and periods. Those elements in the same vertical column belong to the same natural group, while those in the same horizontal row belong to the same period. Selecting from each group the important elements, we have the following distinct families:

| | |
|---|---|
| Group 0. | Inert elements or argon family — helium, neon, argon, krypton, xenon. |
| Group I. | Alkali metals or sodium family — lithium, sodium, potassium. |
| | Univalent heavy metals or copper family — copper, silver, gold. |
| Group II. | Alkaline earth metals or calcium family — calcium, strontium, barium, radium. |
| | Bivalent heavy metals or zinc family — magnesium, zinc, cadmium, mercury. |
| Group III. | Boron family — boron. |
| | Earth metals or aluminium family — aluminium. |
| Group IV. | Tetravalent non-metals or carbon family — carbon, silicon. |
| | Tetravalent metals or tin family — tin, lead. |
| Group V. | Pentavalent non-metals and metals or nitrogen family — nitrogen, phosphorus, arsenic, antimony, bismuth. |
| Group VI. | Hexavalent metals or chromium family — chromium, molybdenum, tungsten, uranium. |
| | Hexavalent non-metals or oxygen family — oxygen, sulphur, selenium, tellurium. |
| Group VII. | Manganese family — manganese. |
| | Halogen elements or chlorine family — fluorine, chlorine, bromine, iodine. |
| Group VIII. | Iron family — iron, cobalt, nickel. |
| | Platinum family — platinum. |

In several of these families the similarity is marked, especially between the alkali metals and also the halogens; in some cases the resemblance is not very striking except in a limited number of properties. So far, our treatment has ignored these groups, brief references only having been made to the argon family. In the succeeding pages, however, the different groups will be emphasized both as to their individual members and their collective properties.

As stated above, the elements in the same horizontal row belong to the same period. The periodic variations of the properties of certain typical elements may be illustrated by the first (I) and second (II) periods. Ignoring the argon family which is somewhat anomalous, and beginning with lithium, the general chemical properties vary regularly with increasing atomic weight. The metallic character typified by lithium gradually diminishes through beryllium and boron; while the feeble non-metallic character typified by carbon increases through nitrogen and oxygen until fluorine is passed and sodium is reached; here the metallic character reappears. Proceeding onward from sodium, the same decrease of basic and increase of acid properties is noticed until potassium is reached, and here again the marked metallic character reappears. There is no sudden change in properties until we pass from one period to the next. Thus, fluorine at the end of the second period forms a strong acid, but sodium at the beginning of the third period forms a strong base. Similarly, chlorine is strongly acidic, but potassium, which is the first metal in the next period, is markedly basic; chlorine is a typical non-metal, while potassium is a typical metal. Not all the periods are as typical as those just cited, but in many cases the progressive change in chemical properties is too obvious to ascribe to mere chance. Many of these relations will be pointed out in the following chapters. Indeed it is hardly possible to

appreciate the full significance of the periodic classification until most of the elements have been studied.

**Periodic Law.** — The relation between properties and atomic weights which brings about this periodic variation is general, and is often summarized in the form of a law known as **the periodic law**, thus : —

*The properties of the elements are periodic functions of their atomic weights.*

Function here means the exhibition of some special relation, viz. that of properties to atomic weight. Interpreted freely, the law means: (1) properties and atomic weight are related, they depend upon each other; and (2) this relation is exhibited repeatedly at regular intervals.

**Conclusion.** — An examination of the table on page 358 shows some imperfections in the periodic classification. For example, there are gaps. These probably correspond to elements not yet discovered or fully investigated. Three such gaps, which were in the original table, have been filled. When Mendelejeff proposed his arrangement, he predicted the discovery of three elements having definite properties. These elements — gallium, scandium, and germanium — have since been discovered, and now occupy their predicted places in the table. Possibly other gaps will be filled by newly discovered elements. Several elements do not fall into their proper places. Thus, the atomic weight of argon indicates that this element should exchange places with potassium. Similarly the positions of iodine and tellurium should be reversed; their properties, however, necessitate the present places. Hydrogen has no appropriate place in the series.

The periodic classification, although imperfect in some particulars, simplifies the study of chemistry, and will be utilized in its larger aspects in many of the following chapters.

# CHAPTER XX

## Fluorine — Bromine — Iodine

Fluorine, bromine, and iodine, together with **chlorine**, constitute a family in the seventh (VII) periodic group, often called the **halogens**. They have similar chemical properties, and form analogous compounds which likewise have similar properties, differing mainly in degree.

Halogen means "sea-salt producer." It is applied to this group of elements because they form salts which are found in sea water and resemble sodium chloride (common salt or sea salt). Chlorides, bromides, fluorides, and iodides are called **halides**. The Greek word for salt, *hals*, suggested these descriptive terms.

Chlorine was fully discussed in Chapter XII.

### Fluorine

**Occurrence.** — Fluorine is the most active of all the halogen elements, and is never found free in nature. It occurs abundantly in combination with calcium as fluor spar or calcium fluoride ($CaF_2$). Other native compounds are cryolite ($Na_3AlF_6$) and apatite ($CaF_2 . 3\,Ca_3(PO_4)_2$). Minute quantities of combined fluorine are found in bones and blood, in the enamel of the teeth, and in sea and some mineral waters.

**The Isolation of Fluorine** was accomplished in 1886 by Moissan, though many unsuccessful attempts had previously been made. He decomposed hydrofluoric acid by electricity, and collected the liberated fluorine. The achievement was

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attended with tremendous difficulties, owing to the intense activity of the fluorine and its corrosive properties.

The essential parts of the apparatus used by Moissan are shown in Figure 56. The U-tube, made of an alloy of platinum and iridium, is provided with tightly fitting stoppers of fluor spar ($S$, $S$). Through the stoppers pass the electrodes ($E$, $E$), of platinum-iridium, held in place by screw caps ($C$, $C$). Side tubes ($T$, $T$) allow the liberated gases (fluorine and hydrogen) to be drawn off separately through platinum delivery tubes. Perfectly dry hydrofluoric acid is put into the U-tube, and dry acid potassium fluoride ($HKF_2$) is added to enable the solution to conduct the current — dry, liquid hydrofluoric acid itself being a non-conductor. The U-tube is then cooled to a low temperature (— 23 to — 50° C.), and on passing a current through the solution fluorine is evolved at the positive electrode (anode) and hydrogen at the negative electrode (cathode). The fluorine freed from hydrofluoric acid vapor was collected by Moissan at first in a platinum tube with a thin fluor spar plate closing each end, so he could look inside and examine the gas. Later he found that the electrolysis could be performed in a copper U-tube and pure dry fluorine could be collected in a glass tube.

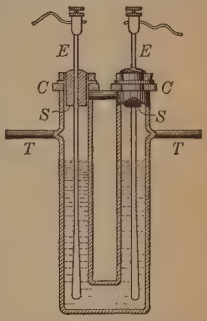


FIG. 56. — Moissan's apparatus for preparing fluorine.

**Properties.** — Fluorine is a gas having a greenish yellow color, though lighter and more yellowish than chlorine. The critical temperature is — 120° C. Subjected to pressure and a sufficiently low temperature, it condenses to a very pale yellow liquid, which boils at about — 187° C. The vapor density shows that the molecular weight is about 38; hence, each molecule contains two atoms and fluorine gas has the formula $F_2$ (the atomic weight being 19).

Chemically fluorine is intensely active. Hydrogen, bromine, iodine, sulphur, phosphorus, carbon, silicon, and boron

take fire in it, but oxygen, nitrogen, and argon do not unite with it. Most metals burn in it, forming fluorides. Gold and platinum are not attacked by it below red heat. Copper becomes coated with copper fluoride, which protects the metal, so that copper vessels may be used as fluorine generators and reservoirs. Moissan used a copper U-tube to prepare large volumes. Water is decomposed by it at ordinary temperatures, while hydrocarbons are instantly decomposed, hydrofluoric acid and carbon fluorides being the important products.

**Hydrofluoric Acid** is the compound of fluorine corresponding to hydrochloric acid. It is prepared by the interaction of a fluoride and concentrated sulphuric acid, just as hydrochloric acid is prepared from a chloride and sulphuric acid. Calcium fluoride is usually used, and the experiment is performed preferably in a lead dish. The chemical change is represented thus : —

| $CaF_2$ | + | $H_2SO_4$ | = | $2\,HF$ | + | $CaSO_4$ |
|---|---|---|---|---|---|---|
| Calcium Fluoride | | Sulphuric Acid | | Hydrofluoric Acid | | Calcium Sulphate |

Pure hydrofluoric acid is a colorless liquid which boils at about 19° C. It is very volatile and is readily transformed into a colorless gas (hydrogen fluoride), which fumes in the air and dissolves in water, the aqueous solution being the commercial hydrofluoric acid. Both gas and solution are dangerous substances. The gas is extremely poisonous, and the liquid, if dropped on the skin, produces terrible sores. Owing to its corrosive action hydrofluoric acid is preserved and sold in hard rubber, lead, or wax bottles. The vapor density of hydrofluoric acid gas varies with the temperature. From 19° to 30° C. the vapor density indicates a molecular weight of 40, while at 88° C. the molecular weight is 20. The atomic weight of fluorine is 19. Hence at the lower

temperature the formula of the gas is $H_2F_2$ and at the higher temperature it is HF.

Hydrofluoric acid interacts with metals, thereby liberating hydrogen and forming fluorides. It also interacts with bases and metallic oxides and forms fluorides. There are two classes of fluorides — normal and acid. Thus, calcium fluoride ($CaF_2$) is a normal salt and hydrogen potassium fluoride ($HKF_2$) is an acid salt.

A solution of hydrofluoric acid and the moist gas both attack glass and are used extensively in etching. The glass is coated with wax, and the design to be etched is scratched through the wax. The glass is then exposed to the gas or liquid, which attacks the unprotected places. When the wax is removed, a permanent etching like the design is left. Glass is an artificial compound of silicon — a silicate. The corrosive action of hydrofluoric acid upon glass is due to the ease with which the acid decomposes glass and forms with silicon a volatile compound, called silicon tetrafluoride ($SiF_4$). Since silicon dioxide (in the form of sand) is an ingredient of the mixture of which glass is made, the equation for the essential chemical change in etching glass may be written thus: —

| $SiO_2$ | + | $4\,HF$ | = | $SiF_4$ | + | $2\,H_2O$ |
|---|---|---|---|---|---|---|
| Silicon Dioxide | | Hydrofluoric Acid | | Silicon Tetrafluoride | | |

Scales on thermometers and on other graduated glass instruments are often etched with hydrofluoric acid.

## Bromine

**Occurrence.** — Bromine is never found free in nature on account of its chemical activity. Bromides are widely distributed, especially sodium bromide and magnesium bromide. The salt springs of Ohio, West Virginia, Pennsylvania, and

FIG. 57. — Apparatus for preparing bromine in the laboratory. Part of the liberated bromine escapes as a vapor and part quickly condenses to a liquid which collects in the V-bend of the delivery tube.

Michigan, and the salt deposits at Stassfurt in Germany furnish the main supply of the element. Sea water, Chili saltpeter ($NaNO_3$), and certain seaweeds contain a small quantity of combined bromine.

**Preparation.** — Bromine is obtained from its native compounds by electrolysis and by treatment with chlorine or with sulphuric acid and some oxidizing agent like potassium chlorate or manganese dioxide. In the laboratory, bromine is prepared by heating potassium bromide with manganese dioxide and sulphuric acid in a glass vessel (Fig. 57). The bromine is easily liberated as a dense, brown vapor, which often condenses to a liquid and runs down the walls of the vessel. The chemical change is represented thus: —

$$\underset{\text{Potassium Bromide}}{2\,KBr} + \underset{\text{Sulphuric Acid}}{2\,H_2SO_4} + \underset{\text{Manganese Dioxide}}{MnO_2} = \underset{\text{Bromine}}{Br_2} + \underset{\text{Manganese Sulphate}}{MnSO_4} + \underset{\text{Potassium Sulphate}}{K_2SO_4} + \underset{\text{Water}}{2\,H_2O}$$

Bromine is sometimes prepared in the laboratory by treating a bromide with manganese dioxide and hydrochloric acid.

The main source of bromine in the United States is "bittern" — a solution containing bromides left after the table salt is crystallized from brine. In the **continuous process** the hot bittern flows down a large tower filled with broken brick or burned clay balls; chlorine gas (frequently obtained by the electrolysis of chlorides) and steam forced in at the bottom meet the bittern and liberate the bromine, which passes as a vapor out of the top into a condenser. The main chemical changes are represented thus: —

$$\underset{\text{Magnesium Bromide}}{MgBr_2} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Bromine}}{Br_2} + \underset{\text{Magnesium Chloride}}{MgCl_2}$$

$$\underset{\text{Sodium Bromide}}{2\,NaBr} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Bromine}}{Br_2} + \underset{\text{Sodium Chloride}}{2\,NaCl}$$

In the **periodic process**, used chiefly in the United States, a huge stone still is charged with manganese dioxide, hot bittern, and sulphuric acid, and heated by steam. The bromine distills into a condenser, as in the other process. Sometimes potassium chlorate is used as the oxidizing agent, and the equation for the essential chemical change is: —

$$\underset{\text{Potassium Chlorate}}{KClO_3} + \underset{\text{Hydrochloric Acid}}{6\,HCl} = \underset{\text{Chlorine}}{3\,Cl_2} + \underset{\text{Potassium Chloride}}{KCl} + \underset{\text{Water}}{3\,H_2O}$$

**Properties.** — Bromine is a heavy, reddish brown liquid at the ordinary temperature. Its specific gravity is about 3. It is a volatile liquid, boiling at about 59° C. The vapor, which is given off freely, has a disagreeable, suffocating odor. This property suggested the name bromine (from the Greek word *bromos*, a stench). It is poisonous, and burns the flesh frightfully. Bromine is somewhat soluble in water. The solution called **bromine water** has a brown color and is sometimes used instead of bromine itself. The solution contains an unstable bromine hydrate. Bromine dissolves in carbon disulphide, and this solution is yellow. Its vapor density up to about 750° C. requires a molecular weight of 160, and since the atomic weight is 79.92, the formula of bromine vapor is $Br_2$.

Bromine combines directly with many elements, especially hydrogen, phosphorus, and metals. The action is not so violent as with chlorine. In fact free chlorine readily displaces bromine from some of its compounds. The chemical properties of bromine can be illustrated by a simple experiment. If powdered magnesium is added to bromine water, the brown color disappears, owing to the formation of colorless magnesium bromide by the direct combination of magnesium and bromine. Upon the addition of chlorine (or chlorine water) to this colorless solution, the brown color reappears, owing to the free bromine which is displaced from the magnesium bromide by the more active chlorine.

**Compounds of Bromine.** — Hydrogen bromide (HBr) is a colorless pungent gas, which fumes in the air and dissolves freely in water, forming a solution usually called hydrobromic acid. Its other properties closely resemble those of hydrochloric acid, though it is less stable than its chlorine analogue. **Bromides** are salts of hydrobromic acid, though many are formed by direct combination with bromine. Most bromides, like the chlorides, dissolve in water. Potassium bromide (KBr) is a white solid, made by decomposing iron bromide with potassium carbonate. It is used extensively as a medicine and in photography (in preparing silver bromide plates and films).

**Miscellaneous.** — Bromine itself is used to make potassium bromide and other compounds, especially certain coal tar dyes.

Balard discovered bromine in 1826 in the mother liquor (or bittern) from brine. Liebig, to whom it was submitted for examination, supposed it was chloride of iodine, and thus failed to discover its elementary nature, because, as he said, he yielded to "explanations not founded on experiment."

## Iodine

**Occurrence.** — Free iodine is never found in nature, but like chlorine and bromine it occurs in combination with metals, especially sodium, potassium, or magnesium. It is widely distributed, though the quantity in any one place is small. Tobacco, water-cress, cod-liver oil, oysters, and sponges contain minute quantities of iodine compounds. Native iodides of silver and of mercury are found. The ash of some seaweeds contains from 0.5 to 1.5 per cent of its weight of iodides of sodium and potassium. Sodium iodate ($NaIO_3$) occurs in the deposits of saltpeter in Chili, and is now the main source of the element.

**Preparation.** — Iodine is prepared in the laboratory by a method similar to that used for bromine. Potassium iodide, manganese dioxide, and sulphuric acid are heated in a glass vessel, and the iodine is liberated as a violet vapor, which quickly condenses on the upper part of the vessel as dark grayish crystals. The equation for the chemical change is —

$$2\,KI + 2\,H_2SO_4 + MnO_2 = I_2 + MnSO_4 + K_2SO_4 + 2\,H_2O$$

Potassium Iodide — Sulphuric Acid — Manganese Dioxide — Iodine — Manganese Sulphate — Potassium Sulphate — Water

On a commercial scale iodine is prepared from the ash of seaweeds and from the mother liquors of Chili saltpeter. (1) Along the coasts of France, Japan, Scotland, and Norway seaweed is collected and burned; sometimes the seaweed is allowed to ferment before being burned in order to convert the complex iodine compounds into non-

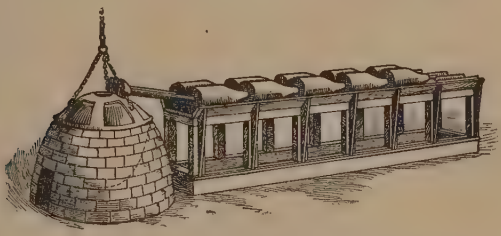


Fig. 58. — Apparatus for purifying iodine.

volatile iodides. From the ash, which is called kelp or varec, the soluble portions are removed by agitation with water. The filtered liquid is further purified, and from the final mother liquor in which the iodides are dissolved the iodine is extracted by heating with sulphuric acid and manganese dioxide. Sometimes chlorine is used to extract the iodine, the equation for this chemical change being —

$$2\,NaI + Cl_2 = I_2 + 2\,NaCl$$

Sodium Iodide — Chlorine — Iodine — Sodium Chloride.

In either case the mother liquor and its added ingredients are distilled gently in an iron pot with a lead cover, which is connected with two rows of bottle-shaped condensers (Fig. 58). The iodine, which

collects in these condensers, is purified by washing and resubliming. (2) In the other process the mother liquor (which contains about 22 per cent of sodium iodate) from the Chili saltpeter is mixed with sodium sulphite and acid sodium sulphite ($HNaSO_3$); the precipitated iodine is collected on coarse cloth, washed, dried, and then resublimed, as described above. The equation for this method of preparation is —

$$\underset{\text{Sodium Iodate}}{2\,NaIO_3} + \underset{\text{Sodium Sulphite}}{3\,Na_2SO_3} + \underset{\text{Acid Sodium Sulphite}}{2\,HNaSO_3} = \underset{\text{Iodine}}{I_2} + \underset{\text{Sodium Sulphate}}{5\,Na_2SO_4} + \underset{\text{Water}}{H_2O}$$

Courtois, a French chemist, discovered iodine in 1812, in an attempt to prepare potassium nitrate from seaweed. Davy and Gay-Lussac established its elementary nature and discovered many of its properties. The present name was given by Davy.

**Properties.** — Iodine is a dark grayish crystalline solid, resembling graphite in luster. It crystallizes in plates which have a specific gravity of about 5. It is volatile at the ordinary temperature, melts at 114° C., and boils at 184° C. When gently heated, the vapor which is formed has a beautiful violet color. This color suggested the name of iodine (from the Greek word *iodes*, violetlike). The vapor is nearly nine times heavier than air. It has an odor resembling that of dilute chlorine, though less irritating. When the vapor is heated, its color changes from violet to deep blue, and the density decreases. Experiment shows that from about 200 to 700° C. the vapor density requires a molecular weight of about 255; since the atomic weight is 126.92, the molecules contain only two atoms and the formula of iodine vapor is $I_2$ up to this temperature. As the temperature rises the molecules dissociate, until at about 1700° C., the vapor consists entirely of atoms. Iodine stains the skin yellow, and turns cold starch solution blue. The presence of a minute trace of iodine may be thus detected, one part of iodine in over 400,000 parts of water producing the blue color. The exact nature of this blue substance is unknown.

The presence of starch in many vegetable substances can be shown by this delicate test. Iodine dissolves slightly in water, and freely in alcohol, chloroform, carbon disulphide, and potassium iodide solution. The chloroform and carbon disulphide solutions are violet, but the others are brown or even black.

The chemical properties of iodine resemble those of chlorine and bromine, but it is less active. It forms no hydrate with water, differing from chlorine and bromine in this respect. Bromine and chlorine displace iodine from its binary compounds, chlorine and chlorine water being often used for this purpose. It combines directly with some non-metals and most metals.

**Compounds of Iodine** resemble the corresponding ones of chlorine and bromine. Hydriodic acid (HI) is much like hydrobromic and hydrochloric. Iodides are salts of hydriodic acid, and like many salts they are prepared in various ways. In general behavior they are similar to bromides and chlorides. Potassium iodide (KI) is prepared and used like potassium bromide.

Brief reference was made in Chapter XI to the equilibrium established when hydriodic acid is formed by heating hydrogen and iodine in a closed tube. The elements begin to combine at about 445° C., while the acid begins to decompose at about 180° C. The reactions proceed in direct and reverse directions, though not to completion, for a condition of equilibrium is soon reached and further accumulation of the products ceases. Chemical change is still going on, but one reaction neutralizes the other. For example, at about 445° C. a condition of equilibrium prevails, both reactions are still in operation, though the tube contains about 79 per cent of hydriodic acid and 21 per cent of hydrogen and iodine. This state of equilibrium is maintained as long

as certain conditions prevail, but like other states of equilibrium it is rather sensitive and is easily displaced by varying the temperature, the pressure, or the concentration of the substances in the tube. The equation expressing the reversible reaction just discussed may be written —

$$H_2 + I_2 \rightleftarrows 2\,HI$$

**Miscellaneous.** — Iodine dissolved in alcohol, in potassium iodide solution, or both, is used (under the name of tincture of iodine) as an application for the skin to prevent the spread of eruptions or to reduce swellings. Iodine is used to make medicinal preparations, especially iodoform ($CHI_3$), which is used as an antiseptic dressing for wounds. Large quantities of iodine are used in making aniline dyes.

**Halogen Family.** — The physical and chemical properties of the halogen elements furnish a typical illustration of the resemblances, differences, and gradation of properties which characterize a family of elements in the same periodic group. If these elements are arranged in the order of their atomic weights, from fluorine (19.0) through chlorine (35.46) and bromine (79.92) to iodine (126.92), the periodic nature of the group is revealed. Thus, the specific gravity increases in this order (*i.e.* fluorine to iodine); the color likewise grows deeper, but the volatility decreases. So also, the melting points of the solidified elements and the boiling points of the liquefied elements increase in this order. Chemically, these elements unite with hydrogen to form analogous compounds, and the intensity of the chemical action decreases gradually as we pass from fluorine to iodine.

The halogen acids resemble each other in their solubility, all (except HF) forming solutions in which the dissociation is large; in other words, they are strong acids. Salts of the

halogen acids often resemble one another, especially those of sodium and potassium, which are white solids, soluble in water, from which they crystallize in cubes.

The valence of the halogens is one toward hydrogen and metals.

### Problems and Exercises

1. What is the percentage composition of (*a*) fluor spar ($CaF_2$) and (*b*) cryolite ($Na_3AlF_6$)?

2. How much (*a*) calcium sulphate and (*b*) hydrofluoric acid are formed by heating 100 gm. of fluor spar with sulphuric acid?

3. Calculate the percentage composition of (*a*) potassium bromide (KBr), (*b*) potassium iodide (KI), (*c*) silver bromide (AgBr), and (*d*) iodoform ($CHI_3$).

4. How much potassium iodide is needed to prepare 63.5 gm. of iodine?

5. How much potassium bromide is needed to prepare 10 gm. of bromine?

6. If 3.946 gm. of silver are needed to precipitate the bromine in 4.353 gm. of potassium bromide, what is the atomic weight of bromine?

7. If the specific gravity of bromine is 3, what volume does one pound occupy?

8. If 63.8351 gm. of silver iodide yield 38.9656 gm. of silver chloride, what is the atomic weight of iodine if 107.88 and 35.46 are accepted as the atomic weights of silver and chlorine respectively?

9. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): Lithium chloride, magnesium iodide, mercurous iodide, mercuric bromide, aurous chloride, auric bromide, barium fluoride, silicon fluoride, platinum chloride, zinc chloride, ferrous bromide, ferric chloride, lead iodide.

10. Write the equations for the following reactions: (*a*) Potassium bromide and silver nitrate form silver bromide and potassium nitrate. (*b*) Sodium iodide and silver nitrate form silver iodide and sodium nitrate.

11. Write the equations in Problem 10 in the ionic form.

## CHAPTER XXI

### Boron

**Occurrence.** — Boron (B) is never found free, but several of its compounds are abundant, *e.g.* borax ($Na_2B_4O_7$), boric acid ($H_3BO_3$), boracite ($(Mg_3B_8O_{15})_2 \cdot MgCl_2$), and colemanite ($Ca_2B_6O_{11} \cdot 5\,H_2O$).

**Boron is prepared** by heating the oxide ($B_2O_3$) with magnesium, aluminium, sodium, or potassium. It is a brown amorphous powder, without taste or odor. It burns when heated in air, forming the oxide ($B_2O_3$) and a nitride (BN). It also unites with the halogens, carbon, and nitrogen. Carbon boride ($CB_6$) is nearly as hard as diamond.

**Boric Acid,** $H_3BO_3$, is contained in the waters and steam of certain volcanic regions, notably Tuscany in Italy. Large basins or tanks are built around these steam jets (called suffioni) and are arranged so that the water flows at intervals from one reservoir into the next lower, constantly becoming charged with more boric acid, as the steam condenses. The final solution is evaporated by aid of the heat from the steam jets, and the crude boric acid which settles out is purified by recrystallization. This compound is sometimes called boracic acid. Boric acid is made in the United States from borax and colemanite, and in Germany from the boracite found at Stassfurt. The essential feature of the process is a decomposition of the mineral into boric acid by an inorganic acid. The following equation illustrates the transformation: —

$$\underset{\text{Borax}}{Na_2B_4O_7} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{H_2SO_4} + 5\,H_2O = \underset{\text{Boric Acid}}{4\,H_3BO_3} + \underset{\substack{\text{Sodium}\\\text{Sulphate}}}{Na_2SO_4}$$

Boric acid crystallizes in lustrous, white flakes, which feel greasy. It dissolves slightly in cold water, readily in hot water and in alcohol. When the alcoholic solution is burned, a boron compound colors the vapor green. This is a **test for boron compounds.**

Boric acid is used in making borax, in the manufacture of enamels and glazes for pottery, as an antiseptic in medicine and surgery, and for preserving meat, fish, milk, butter, beer, and wine.

When boric acid is heated, it loses water and is transformed into metaboric acid ($HBO_2$) at 100° C. and tetraboric acid ($H_2B_4O_7$) at 140° C. Boric acid forms no salts, but the other acids do, the best-known salt being sodium tetraborate or borax.

**Borax**, $Na_2B_4O_7$, occurs native in California, and an impure borax called tinkal comes from the East. Most of the commercial borax is made from calcium borate (colemanite, $Ca_2B_6O_{11} \cdot 5\,H_2O$) by boiling with sodium carbonate and separating the borax by crystallization.

Borax is a white crystalline solid and has five or ten molecules of water of crystallization, depending upon the temperature at which crystallization occurs. The crystals

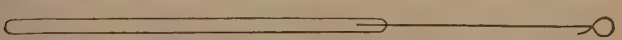


Fig. 59. — Looped platinum wire for making tests with borax beads.

containing ten molecules of water are prismatic, those containing five are octahedral. Commercial borax is the powdered form of the crystals, usually the prismatic. It effloresces in the air. Consequently, when heated, borax melts and swells (as the water of crystallization escapes) into a white porous mass, which finally becomes a glassy solid. If the borax is melted on the end of a looped platinum wire, the transparent globule is called a borax bead (Fig. 59). This

glassy borax dissolves metallic substances, especially metallic oxides. These beads may be made to assume different colors characteristic of the metals, when the beads are heated with the oxides or solutions of different metals. The following table shows the —

COLORS OF BORAX BEADS

| METAL | OXIDIZING FLAME | | REDUCING FLAME | |
|---|---|---|---|---|
| | Hot | Cold | Hot | Cold |
| Chromium | Reddish yellow | Yellowish green | Green | Green |
| Cobalt | Blue | Blue | Blue | Blue |
| Copper | Green | Greenish blue | Colorless | Red |
| Manganese | Violet | Violet | Colorless | Colorless |

The bead test is often used in chemistry to confirm other observations or to suggest further examination. The chemical changes in borax beads can be readily understood if borax is regarded as a mixture of sodium metaborate and boron trioxide ($2\,NaBO_2 + B_2O_3$); the acid oxide ($B_2O_3$) unites with the basic (*i.e.* metallic) oxides and forms a colored borate. For example, with copper oxide a green bead is obtained which is $2\,NaBO_2 . Cu(BO_2)_2$.

A solution of borax has an alkaline reaction, because borax hydrolyzes with water and boric acid is only slightly ionized.

Large quantities of borax are used in the manufacture of enamels and glazes, especially those which form the protective coating of domestic utensils. Considerable is used for preserving canned meat and fish. It is a cleansing agent, and large quantities are consumed in laundries as well as in the manufacture of soap, particularly the variety intended for use in hard water. (See Soap and Hard Water.) The property of dissolving oxides adapts borax for use in soldering certain metals. Solder adheres only to clean metals, so a

little borax is used to dissolve the film of oxide on the surfaces to be joined. It also finds use as a mordant in calico printing and in dyeing, and in the manufacture of water-soluble varnishes. It is an ingredient of the ointments, lotions, and powders which are designed to relieve hoarseness or skin eruption.

**Miscellaneous.** — Boron is a non-metal and belongs to the aluminium family in the third periodic group (III), but chemically it closely resembles carbon and silicon and their compounds. Its valence is three.

### Problems

1. What per cent of borax ($Na_2B_4O_7 . 10\ H_2O$) is boron?
2. Write the equations for the transformation of boric acid into metaboric and tetraboric acids; and the equation for the formation of boron trioxide from tetraboric acid.
3. How many grams of $H_3BO_3$ are formed by the interaction of water, sulphuric acid, and 782 gm. of borax?
4. Calculate the per cent of boron in (*a*) colemanite, and (*b*) boracite.

## CHAPTER XXII

### Silicon — Glass

**Occurrence.** — Silicon does not occur free in nature, being found almost exclusively as silicon dioxide ($SiO_2$) or as silicates. These compounds are so abundant and widely distributed that approximately one fourth of the earth's crust is silicon. Sand and the different varieties of quartz are silicon dioxide, while many rocks are silicates.

**Preparation and Properties.** — Silicon is no longer a rare element. It is prepared by heating a special mixture of silicon dioxide and carbon in an electric furnace at a temperature which is carefully regulated to prevent loss of the silicon by volatilization or combination with the carbon. The equation for the chemical change is —

$$\underset{\text{Silicon Dioxide}}{SiO_2} + \underset{\text{Carbon}}{2C} = \underset{\text{Silicon}}{Si} + \underset{\text{Carbon Monoxide}}{2CO}$$

Thus prepared silicon is a gray-black, lustrous, massive solid. It melts at about 1400° C. and oxidizes to silicon dioxide when heated to about this temperature. The specific gravity is about 2.37, and the hardness is between six and seven (*i.e.* between orthoclase and quartz).

Silicon is also obtained as a brown amorphous powder by heating a mixture of powdered magnesium and silicon dioxide, and as dark steel-colored crystals by dissolving the amorphous variety in melted zinc or lead.

**Silicon Dioxide** or **Silica**, $SiO_2$, is the most common compound of silicon. It occurs native in both crystalline and

amorphous conditions, but when produced by a chemical process in the laboratory it is usually a white amorphous powder. Sand, gravel, sandstone, and quartzite are almost wholly silica. It is an essential ingredient of many rocks, as granite and gneiss. **Quartz** is silicon dioxide. Pure crystalline quartz is colorless and transparent, and is frequently found as crystals which consist usually of a six-sided prism with a six-sided pyramid at one or both ends; but the crystals are often distorted or complex (Fig. 60). There are many varieties of quartz, which differ in color and structure, due to minute impurities or to the mode of formation. Among the crystalline varieties are the clear, colorless rock crystal, the purple amethyst, and the rose, yellow, glassy, milky, and smoky forms. Varieties imperfectly crystalline or amorphous are the waxlike chalcedony, the various forms of agate having different colored layers, the reddish brown carnelian, the black and white onyx, the red or brown jasper, the dull brown or black flint, and the brittle chert. Opal is hydrated silica ($SiO_2 . n H_2O$). Petrified or silicified wood is largely some variety of quartz which has replaced the woody fiber. Infusorial or diatomaceous earth is a variety of silica consisting of the shells of minute organisms called diatoms.

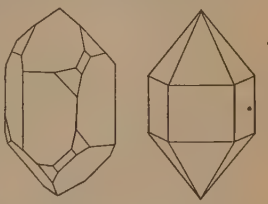


Fig. 60. — Quartz crystals.

Quartz crystals and most crystalline varieties of silica are hard enough to scratch glass. They are insoluble in water and acids, except hydrofluoric acid, but are transformed into a soluble alkaline silicate when heated in the hydroxides or carbonates of sodium and potassium. Thus, when fine sand is fused with sodium carbonate the equation for the reaction is —

| $Na_2CO_3$ | + | $SiO_2$ | = | $Na_2SiO_3$ | + | $CO_2$ |
|---|---|---|---|---|---|---|
| Sodium Carbonate | | Silicon Dioxide | | Sodium Silicate | | Carbon Dioxide |

Silica itself is infusible, except in the oxyhydrogen flame and electric furnace. If pure silica is fused with certain precautions, the molten mass can be shaped into elastic threads, which are used to suspend delicate parts of electrical instruments, and into tubes, flasks, crucibles, etc., which do not crack by sudden heating and cooling. The specific gravity of quartz is about 2.65.

Sandstone and quartzite are used as building stones, and hard sandstone is made into grindstones and whetstones. Sand is used in making sandpaper, glass, porcelain, and mortar. Glass is roughened and cut by blowing or "blasting" fine sand against it. Many of the varieties of quartz are cut and polished into ornaments and gems, *e.g.* amethyst, opal, and agate. Rock crystal is used as the "diamond" in cheap jewelry, and is sometimes cut into lenses for eyeglasses and optical instruments. Petrified wood is cut and polished into table tops, mantelpieces, and fireplaces. Infusorial earth is used to polish silver ("electro-silicon" being the commercial name of one kind) and in making cement, "soluble glass," dynamite, and refractory brick.

**Silica and Plants.** — The ash of many plants contains silica, showing that some compound of silicon is assimilated by the plant from the soil — probably silicic acid or a soluble silicate (see below). The ash of rye and wheat straws and of potato stems contains from 40 to 70 per cent of silica. Plants like horsetail and bamboo are rich in silica. The silica is probably not a plant food in the strict sense, but gives firmness to the tall stalks, especially to their joints.

**Silicic Acids and Silicates.** — Silicon being a non-metal forms acids, many of which are complex and known only

through the corresponding salts. The two which are simple and best known are metasilicic acid ($H_2SiO_3$) and orthosilicic acid ($H_4SiO_4$). As stated in a preceding paragraph, sodium silicate ($Na_2SiO_3$) is formed when silicon dioxide is fused with sodium carbonate. Now sodium silicate dissolves in water, and when hydrochloric acid is added to a concentrated solution, a silicic acid is precipitated as a white gelatinous mass. The precipitate is probably orthosilicic acid, but when this precipitate is dried only metasilicic acid is found in the residue, thus: —

$$\underset{\text{Orthosilicic Acid}}{H_4SiO_4} = \underset{\text{Metasilicic Acid}}{H_2SiO_3} + \underset{\text{Water}}{H_2O}$$

The metasilicic acid on further heating decomposes into silicon dioxide and water, thus: —

$$\underset{\text{Metasilicic Acid}}{H_2SiO_3} = \underset{\text{Silicon Dioxide}}{SiO_2} + \underset{\text{Water}}{H_2O}$$

It appears then that these two silicic acids are closely related. Indeed orthosilicic acid may be regarded as a sort of parent of the other silicic acids, which, although they have not been isolated, may be conveniently thought of as molecules of orthosilicic acid minus one or more molecules of water. Following out this relationship we have for example the following hypothetical silicic acids: —

$2\,H_4SiO_4 - H_2O = H_6Si_2O_7$, or Disilicic Acid
$3\,H_4SiO_4 - 4\,H_2O = H_4Si_3O_8$, or Trisilicic Acid

Salts of these acids are well-known minerals. (See Silicates, below.)

**Colloids.** — Sodium silicate and hydrochloric acid do not always interact as described under Silicic Acids. If the

sodium silicate solution is dilute, or the hydrochloric acid concentrated or in excess, or the mixing is done quickly, then the silicic acid is formed, but remains in solution. This solution, however, is not a solution of the gelatinous silicic acid described above, for the latter is insoluble in water. Again, if this solution is evaporated, the silicic acid separates as a gelatinous mass which will not redissolve upon the addition of water. The behavior of a solution of silicic acid is referable to the fact that silicic acid does not crystallize, but belongs to a class of jellylike substances called colloids. Glue, gelatine, starch, and albumen are also colloids, and their solutions, known as colloidal solutions, have different properties from ordinary solutions of the well-known crystallizable substances (or crystalloids, as Graham called them). Colloids can be separated by dialysis from the crystalloids in the same solution. Thus, if the solution of silicic acid (prepared from sodium silicate and hydrochloric acid) is placed in a vessel having a bottom of parchment or bladder and hanging in a larger receptacle filled with water, the silicic acid will be retained in the smaller vessel but the sodium chloride will pass through the parchment into the water; if the liquid in the larger vessel is occasionally replaced by water, all the sodium chloride can be removed by this process from the silicic acid.

Colloidal solutions in all probability are really not solutions at all, but liquids in which the colloid is suspended as very fine particles, too fine to be retained by filter paper. This view is substantiated by the fact that the boiling point and freezing point of a colloidal solution are very nearly the same as those of the pure solvent. Many substances insoluble in water form colloidal suspensions, *e.g.* aluminium hydroxide, ferric hydroxide, sulphides, and such metals as copper, gold, and platinum. These are still farther removed from true solutions, and are doubtless little more than exceedingly

fine particles of solid matter uniformly distributed throughout the solvent. This subject is still under investigation.

**Silicates** are the salts of silicic acids, though their corresponding acids have not been isolated in most cases. Sodium and potassium silicates are salts of the well-known metasilicic acid ($H_2SiO_3$). They are the only silicates soluble in pure water, and the thick, sirupy solution of each (or both) is called water glass. It finds extensive use in the manufacture of soap, certain cements, artificial stone, and fireproof materials. As already stated many rocks and minerals are silicates and make up a large part of the earth's crust. The following list shows the relations of a few silicates to their acids: —

| | |
|---|---|
| Metasilicates (Salts of $H_2SiO_3$) | Wollastonite, $CaSiO_3$<br>Enstatite, $MgSiO_3$<br>Beryl, $Be_3Al_2(SiO_3)_6$ |
| Orthosilicates (Salts of $H_4SiO_4$) | Zircon, $ZrSiO_4$<br>Kaolin, $H_2Al_2(SiO_4)_2 . H_2O$<br>Olivine, $Mg_2SiO_4 . Fe_2SiO_4$ |
| Disilicate (Salt of $H_6Si_2O_7$) | Serpentine, $Mg_3Si_2O_7 . 2\,H_2O$ |
| Trisilicate (Salt of $H_4Si_3O_8$) | Orthoclase, $KAlSi_3O_8$ |

Other silicates are mica, hornblende, augite, slate, talc, lava, feldspars related to orthoclase, asbestos, garnet, and tourmaline. The most abundant are the silicates of calcium, aluminium, magnesium, potassium, sodium, and iron.

Silicic acid is a feeble acid. It does not redden blue litmus nor liberate hydrogen when added to magnesium. Nevertheless it is properly called an acid because it forms salts. These salts, which we have already seen make up a large part

of the earth's crust, are slowly decomposed by carbonic acid, *i.e.* by the joint action of the carbon dioxide and water vapor in the atmosphere. This disintegration of the silicates is called weathering.

The water of many hot springs, as in the Yellowstone Park, contains alkaline silicates; and when the solution comes to the surface, some of the silicate is decomposed by the carbon dioxide in the air, and the silica is deposited around the spring in beautiful forms called geyserite or siliceous sinter.

**Silicon Tetrafluoride**, $SiF_4$, is a colorless gas which has a pungent, suffocating odor. It is formed when hydrofluoric acid interacts with silicon dioxide or silicates. Thus, with silicon dioxide the equation is —

$$\underset{\substack{\text{Silicon}\\\text{Dioxide}}}{SiO_2} + \underset{\substack{\text{Hydrofluoric}\\\text{Acid}}}{4\,HF} = \underset{\substack{\text{Silicon}\\\text{Tetrafluoride}}}{SiF_4} + 2\,H_2O$$

Silicon tetrafluoride forms fumes in moist air and interacts readily with water, thus: —

$$\underset{\substack{\text{Silicon}\\\text{Tetrafluoride}}}{3\,SiF_4} + 3\,H_2O = \underset{\substack{\text{Silicic}\\\text{Acid}}}{H_2SiO_3} + \underset{\substack{\text{Hydrofluosilicic}\\\text{Acid}}}{2\,H_2SiF_6}$$

The hydrofluosilicic acid (sometimes called simply fluosilicic acid) remains in solution, while the silicic acid is precipitated. The formation of the white gelatinous silicic acid when the gases from the interaction of hydrofluoric acid and a compound of silicon are led into water is often used as a **test for silicon.**

**Siloxicon** is the commercial name of a highly refractory substance produced by heating a mixture of silicon dioxide and carbon to about 2500° C. in a special form of an electric

furnace. It is not a definite compound, but varies in composition from $Si_2C_2O$ to $Si_7C_7O$. It is a gray-green, granular powder which can be readily shaped into bricks, linings, and other forms of refractory articles.

**Silicides** are compounds of silicon and other elements. Carborundum or carbon silicide is the most important.

**Carborundum**, SiC, is a crystalline compound consisting solely of silicon and carbon. It varies in color from white to emerald green and is sometimes iridescent. It is extremely hard, being nearly as hard as diamond. The specific gravity is about 3. Acids do not affect it, but it is decomposed by fusing it with potassium hydroxide and other alkalies.

Its extreme hardness has led to its application as an abrasive, and large quantities are made into a great variety of grinding wheels, whetstones, and polishing cloths.

Carborundum is manufactured by fusing a mixture of sand and coke in an electric furnace constructed on the resistance type (Fig. 61). It is essentially an oblong box with permanent ends and loosely built sides. Each end is provided with a heavy metal plate. The wires for the electric current are attached to the outer ends of these plates, while the huge carbon electrodes fit into the inner ends, and project into the furnace. A cylindrical mass of granulated coke makes an electrical connection between the electrodes. The mixture of sand and coke (to which salt and sawdust are added to contribute to the fusion and porosity) is packed around this core inside the box. The heat generated by the resistance of the carbon core to the passage of the powerful current of electricity produces a chemical change essentially as follows: —

$$\underset{\text{Sand}}{SiO_2} + \underset{\text{Carbon}}{3\,C} = \underset{\text{Carborundum}}{SiC} + \underset{\substack{\text{Carbon}\\\text{Monoxide}}}{2\,CO}$$

FIG. 61. — Carborundum furnace.

The change is due solely to the intense heat, *i.e.* it is an electrothermal, not an electrolytic change. When the operation is over and the furnace is cool, the side walls are pulled down, and the carborundum is removed. The purest grade

is found around the core. The product is crushed, treated with sulphuric acid to remove the impurities, washed, dried, and graded according to the size of the particles.

**Miscellaneous.** — Silicon is a non-metallic element and belongs to the carbon family in the fourth (IV) periodic group. Certain physical properties suggest a metallic character, but chemically silicon is very closely related to carbon. Both have allotropic modifications and form analogous compounds, *e.g.* $CO_2$ and $SiO_2$, $CH_4$ and $SiH_4$. Both form many compounds of great importance, so that we might conveniently regard silicon as the chief element in the mineral kingdom, just as carbon is in the organic realm.

Silicon has the valence of four in its compounds.

## Glass

Glass is an amorphous, more or less transparent solid. It consists of one or more insoluble silicates with an excess of silica. Glass is not made by mixing silicates, but by fusing a mixture of sand, an alkali, and a calcium or lead compound. The alkali is potassium carbonate ($K_2CO_3$) or sodium carbonate ($Na_2CO_3$), though sodium sulphate and sodium nitrate are used in some cases as auxiliary substances; the calcium compound is limestone ($CaCO_3$) or lime ($CaO$); and the lead compound is litharge ($PbO$) or red lead ($Pb_3O_4$). Besides these fundamental ingredients, small quantities of other substances are used, *e.g.* (1) broken glass (called cullet), which lowers the melting point of the mixture; (2) arsenic trioxide ($As_2O_3$), which destroys carbonaceous impurities; (3) carbon, which lowers the melting point when sodium sulphate is used and likewise imparts a color from straw to amber; and (4) manganese dioxide ($MnO_2$), which neutralizes the green color caused by iron compounds (often present in impure materials).

The process consists in melting a carefully prepared mixture of the proper ingredients in a refractory fire-clay pot. The heat is often obtained by burning gas — manufactured or natural. During the melting, gases escape, and the impurities, which rise to the surface as a scum, are removed. The molten mass is allowed to cool until it has the proper consistency. A portion is then collected as a soft ball on the end of an iron tube and brought to the desired shape, either by forcing it into a mold or by blowing into the tube and simultaneously manipulating the plastic mass by twisting and swinging. The details of the procedure, however, vary with the article being made. Many objects, such as tumblers and small dishes, are now made by pressing the plastic glass with a die or by blowing it into a mold. Fruit jars, bottles, and lamp chimneys are blown by machinery.

All glass must be cooled slowly to prevent brittleness. This operation is called annealing, and is accomplished by passing the objects slowly through a furnace in which the temperature is gradually lowered.

There are four possible kinds of glass and many varieties of each. Their properties depend upon the proportion of the ingredients, and each kind may be made to approach the others in properties by varying these proportions. Arranged in the order of their fusibility and beginning with the softest, the four kinds of glass are: (1) Sodium-lead glass, (2) potassium-lead glass, (3) sodium-calcium glass, and (4) potassium-calcium glass. Flint glass is a lead glass; it is lustrous, refracts light to a high degree, and is made into ornaments and lenses for optical instruments. Certain varieties of flint glass are exceptionally brilliant; they are called strass or paste and are made into artificial gems. Cut glass is a lead glass. Window, plate, crown, table, and bottle glass is a sodium-calcium glass; it is sometimes called

soda glass or soft glass to distinguish it from the potassium-calcium glass, which is hard.

Window glass is made by blowing a lump of glass into a hollow globe and then into a cylinder; this, on being opened at both ends and cut lengthwise, spreads out flat. Plate glass is made by pouring the molten glass upon a large table, rolling it with a hot iron roller, and subsequently grinding and polishing it until the surfaces are parallel. Plate glass is used for large windows and for mirrors, but considerable rough plate is used for skylights and floors. Crown glass is a superior quality of window glass. It has a brilliant surface and is used as "bull's-eyes" in decorative windows and as lenses for optical instruments (in conjunction with flint glass). Most chemical glassware is sodium-calcium glass. It therefore softens when heated and the flame becomes yellow from the sodium. Bohemian or hard glass is a potassium-calcium glass. It is much harder than the other kinds and is used in making chemical apparatus designed to withstand great heat. Soft glass is slightly soluble in water, but hard glass is less so, hence special varieties of hard glass are often made into apparatus which resists the solvent action of water and chemical reagents; Jena glass is one variety.

Glass is colored by adding different substances to the molten mass. Iron, chromium, and certain copper compounds make it green, the green color of many bottles and fruit jars being due to iron compounds in the impure materials used; cobalt compounds produce different shades of blue; manganese dioxide gives a pink or a violet color; yellow is produced by charcoal, sulphur, uranium compounds, or silver; cuprous oxide ($Cu_2O$) and compounds of gold together with a reducing agent give a ruby color; translucent or white glass is made by adding fluor spar or cryolite; stained glass is ordinary glass to which fusible pigments are applied with a brush and then fixed by heat; iridescent glass is made

by secret processes, though it is known that one consists in exposing a special variety of absorbent glass to the vapors of metallic oxides.

### Problems and Exercises

1. Calculate the per cent of silicon in (*a*) quartz, (*b*) willemite ($Zn_2SiO_4$), steatite ($Mg_3Si_4O_{11} . H_2O$).

2. How much carborundum can be made (theoretically) from a ton of sand? (Equation is $SiO_2 + 3\,C = SiC + 2\,CO$.)

3. Calculate the percentage composition of (*a*) carborundum, (*b*) silicic acid ($H_2SiO_3$), (*c*) sodium silicate ($Na_2SiO_3$).

4. Calculate the atomic weight of silicon from the following data: (*a*) 2.621 gm. of silicon tetrachloride ($SiCl_4$) required 6.6445 gm. of silver for precipitation of the chlorine; the atomic weight of silver was accepted as 107.88. (*b*) 95.52367 gm. of silicon tetrabromide ($SiBr_4$) yielded 16.56868 gm. of silicon dioxide; the atomic weights of oxygen and bromine were accepted as 16 and 79.92 respectively.

5. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): Silicon iodide, hydrogen silicide, silicon sulphide, carbon silicide.

# CHAPTER XXIII

## Phosphorus, Arsenic, Antimony, and Bismuth

Phosphorus, arsenic, antimony, and bismuth, together with nitrogen, belong to the nitrogen family in the fifth (V) periodic group of elements.

### Phosphorus

**Occurrence.** — Free phosphorus (P) is not found in nature. But phosphates are numerous and abundant, the most common being phosphorite (impure $Ca_3(PO_4)_2$) and apatite ($3\ Ca_3(PO_4)_2 . CaCl_2$ or $CaF_2$). About .1 per cent of the earth's crust is phosphorus. Calcium phosphate is present in all fertile soils, being a product of decayed rocks. Phosphorus compounds are essential constituents of plants and of the brains, nerves, and bones of animals.

Phosphorus was discovered in 1669 by Brand, a German alchemist, who obtained it by heating a certain kind of animal matter. Scheele, in 1771, extracted it from bones.

**Preparation.** — Phosphorus is prepared industrially by two processes: (1) In the older process bone ash (which is over 80 per cent calcium phosphate) or a native phosphate is finely ground and mixed in large vats with enough sulphuric acid to produce the following change: —

| $Ca_3(PO_4)_2$ | + | $3\ H_2SO_4$ | = | $2\ H_3PO_4$ | + | $3\ CaSO_4$ |
|---|---|---|---|---|---|---|
| Calcium Phosphate | | Sulphuric Acid | | Phosphoric Acid (Ortho-) | | Calcium Sulphate |

The insoluble calcium sulphate is removed by filtering the mixture through cinders. The phosphoric acid solution is

concentrated, mixed with sawdust, coke, or charcoal, and dried, being changed thereby into metaphosphoric acid according to the equation: —

$$\underset{\text{Phosphoric Acid (Ortho-)}}{H_3PO_4} = \underset{\text{Phosphoric Acid (Meta-)}}{HPO_3} + H_2O$$

The dried mass is heated to a high temperature in clay retorts arranged in tiers (Fig. 62), the change thus produced being substantially —

$$\underset{\text{Phosphoric Acid (Meta-)}}{4\,HPO_3} + \underset{\text{Carbon}}{12\,C} = \underset{\text{Phosphorus}}{P_4} + \underset{\text{Hydrogen}}{2\,H_2} + \underset{\text{Carbon Monoxide}}{12\,CO}$$

The phosphorus distills as a vapor through a pipe into a trough of water, where it collects

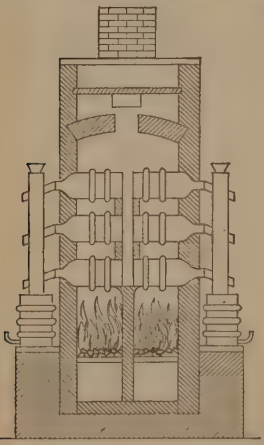


Fig. 62. — Apparatus for the manufacture of phosphorus by the old method (final stage).

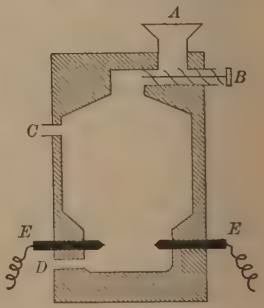



Fig. 63. — Electric furnace for the manufacture of phosphorus. The raw materials introduced at *A* are fed in by the screw *B*, the phosphorus vapor escapes at *C*, and the slag is drawn off at *D*. The electrodes are *E*, *E*.

as a heavy liquid. (2) By a new process phosphorus is manufactured in an electric furnace (Fig. 63). A mixture

of phosphate, carbon, and sand is fed continuously into a furnace provided with an outlet pipe near the upper part through which the phosphorus vapor passes into a condenser. The residue is drawn off as a slag at the bottom of the furnace. The process is an electrothermal one, the essential equation for the chemical change being —

$$\underset{\text{Calcium Phosphate}}{2\ Ca_3(PO_4)_2} + \underset{\text{Sand}}{6\ SiO_2} + \underset{\text{Carbon}}{10\ C} = \underset{\text{Phosphorus}}{P_4} + \underset{\text{Carbon Monoxide}}{10\ CO} + \underset{\text{Calcium Silicate}}{6\ CaSiO_3}$$

Each method gives a black product, which is purified by redistillation in an iron retort, or by oxidation under water with sulphuric acid and potassium dichromate; finally it is pressed through canvas bags and molded into sticks.

**Properties.** — Phosphorus has three allotropic modifications, — yellow or ordinary, red, and black. **Ordinary phosphorus** when freshly prepared is a yellow, translucent solid, but the color deepens by exposure to light. At ordinary temperatures it is like wax, but at low temperatures it is brittle. Under water it melts at 44° C. Exposed to the air, it immediately gives off white fumes, and at 34° C. takes fire and burns with a brilliant flame, the main product being phosphorus pentoxide ($P_2O_5$). It is luminous in moist air, as may be easily seen by rubbing the head of a "sulphur match" in a dark room. This property gave the element its name (from the Greek word *phosphoros*, light bringer). The ease with which it ignites makes phosphorus dangerous to handle. Phosphorus is kept beneath water, and should never be handled or cut unless so covered. Burns from it are severe and hard to heal. It is very poisonous, and the workmen in phosphorus factories are subject to a dreadful disease, which rots the bones. A fatal dose is about .15 gm. It is nearly insoluble in water, but dissolves in carbon disulphide and slightly in sodium hydroxide

solution. Yellow phosphorus has a faint but characteristic odor, which may be easily detected by smelling the head of a "sulphur match." **Red phosphorus** is made by heating ordinary phosphorus to about 250° C. in a closed vessel freed from air. Conversely, if red phosphorus is distilled and the vapor condensed quickly, the yellow variety is obtained. This variety of phosphorus is usually a dark red powder, though sometimes it is a brittle mass. It is opaque and odorless, does not glow or take fire when exposed to the air, and does not ignite until heated to 260° C. It is not poisonous, and does not dissolve in carbon disulphide. It can be handled without danger and need not be kept beneath water. Obviously it is the less active variety of the element.

Black phosphorus is formed by dissolving red phosphorus in melted lead, and allowing crystals to separate.

Certain rat and bug poisons contain yellow phosphorus, but most of the phosphorus of commerce is consumed in the manufacture of matches (see below).

The vapor density of yellow phosphorus is practically constant up to nearly 1500° C. and corresponds to the molecular weight 128. Since the atomic weight is 31, the molecular formula is $P_4$. At higher temperatures partial dissociation occurs. The formula of dissolved phosphorus is also $P_4$.

**Oxides of Phosphorus.** — The two important oxides are phosphorous or the trioxide ($P_2O_3$ or $P_4O_6$) and phosphoric or the pentoxide ($P_2O_5$ or $P_4O_{10}$). **Phosphorous oxide** is a white solid formed by the slow oxidation of phosphorus or by burning phosphorus in a limited supply of air. It has the odor of phosphorus and is poisonous. Warmed in the air, it changes into the pentoxide. It unites with water to form phosphorous acid, thus: —

$$\underset{\text{Phosphorous Oxide}}{P_2O_3} + 3\,H_2O = \underset{\text{Phosphorous Acid}}{2\,H_3PO_3}$$

**Phosphoric oxide** is a white, snowlike solid formed by burning phosphorus in an abundant supply of air. It is very deliquescent and is often used in the laboratory to dry gases. It combines vigorously with cold water, forming metaphosphoric acid, thus: —

$$\underset{\text{Phosphoric Oxide}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric Acid}}{2\,HPO_3}$$

**Acids and Salts of Phosphorus.** — There are three phosphoric acids, — orthophosphoric ($H_3PO_4$), metaphosphoric ($HPO_3$), and pyrophosphoric ($H_4P_2O_7$). Phosphorous acid ($H_3PO_3$) and hypophosphorous ($H_3PO_2$) are less important compounds.

**Orthophosphoric Acid** is a by-product in the manufacture of phosphorus from bone ash (see above); it can be prepared by oxidizing red phosphorus with dilute nitric acid, or by dissolving phosphorus pentoxide in hot water, thus: —

$$\underset{\text{Phosphorus Pentoxide}}{P_2O_5} + 3\,H_2O = \underset{\text{Orthophosphoric Acid}}{2\,H_3PO_4}$$

It is a white deliquescent solid which is very soluble in water.

**Metaphosphoric Acid** is formed by heating orthophosphoric acid to a high temperature, thus: —

$$\underset{\text{Orthophosphoric Acid}}{H_3PO_4} = \underset{\text{Metaphosphoric Acid}}{HPO_3} + H_2O$$

It can be formed by dissolving the pentoxide in cold water, thus: —

$$P_2O_5 + H_2O = 2\,HPO_3$$

At ordinary temperature it is a glassy solid, and is called **glacial phosphoric acid.** It dissolves readily in water, and

the solution changes into orthophosphoric acid — slowly in the cold, rapidly when boiled.

**Pyrophosphoric Acid** is formed by heating orthophosphoric acid or one of its salts to 200°–300° C., thus: —

$$\underset{\text{Orthophosphoric Acid}}{2\,H_3PO_4} = \underset{\text{Pyrophosphoric Acid}}{H_4P_2O_7} + H_2O$$

A sodium salt ($HNa_2PO_4$) of the ortho-acid is usually used. This acid is an amorphous, glassy (but sometimes crystalline) solid, readily soluble in water.

The acids of phosphorus just discussed form salts called **phosphates**, many of which are found as minerals, especially phosphates of calcium, aluminium, and magnesium. The bones of animals and ashes of plants contain calcium and magnesium phosphates. Orthophosphoric acid is tribasic, and its salts, which are usually called simply phosphates, are numerous. They are known as primary, secondary, and tertiary phosphates, according as one, two, or three atoms of hydrogen are replaced. The most important is the normal calcium salt $Ca_3(PO_4)_2$, which has already been described. Hydrogen disodium phosphate ($HNa_2PO_4$) is the commercial sodium phosphate; it is a secondary phosphate. This salt and hydrogen sodium ammonium phosphate, or **microcosmic salt** ($HNa(NH_4)PO_4$), are used in chemical analysis. The "acid phosphate" sold as a beverage is a solution of one or more acid calcium phosphates ($HCaPO_4$ and $H_4Ca(PO_4)_2$). **Metaphosphates** are formed by heating primary (or mono-) sodium phosphates, thus: —

$$\underset{\text{Primary Sodium Phosphate}}{H_2NaPO_4} = \underset{\text{Sodium Meta-phosphate}}{NaPO_3} + H_2O$$

Microcosmic salt when fused also forms a metaphosphate ($NaPO_3$) owing to the loss of water and ammonia ($NH_3$). The

glassy residue is called a phosphorus bead and like the borax bead assumes different colors when heated with metallic oxides. **Pyrophosphates** (of which only two classes are known) are formed by heating secondary (or di-) phosphates, thus: —

$$\underset{\text{Disodium Phosphate}}{2\,HNa_2PO_4} = \underset{\text{Sodium Pyrophosphate}}{Na_4P_2O_7} + H_2O$$

**Hypophosphites** are the salts of hypophosphorous acid and are produced by treating phosphorus with an alkali. They are often used as medicines.

Orthophosphoric acid dissociates mainly into the ions $H^+$ and $H_2PO_4^-$. The disodium phosphate ($HNa_2PO_4$) dissociates into the ions $2\,Na^+$ and $HPO_4^{--}$. Its solution is slightly alkaline because hydroxyl ions are left when the hydrogen ion of the slightly dissociated water forms the $H_2PO_4$-ion with the $HPO_4$-ion, the latter ion having only a very slight, if any, tendency to dissociate; the simple ionic equation for the hydrolysis is —

$$H^+ + OH^- + HPO_4^{--} \rightarrow OH^- + H_2PO_4^-$$

**Tests for Phosphates.** — Soluble phosphates can be detected and distinguished by silver nitrate. Orthophosphates give yellow silver phosphate ($Ag_3PO_4$), metaphosphates give white silver metaphosphate ($AgPO_3$), pyrophosphates give white silver pyrophosphate ($Ag_4P_2O_7$); all dissolve in ammonium hydroxide, but silver metaphosphate dissolves in an excess of an alkaline metaphosphate, while silver pyrophosphate is insoluble. Orthophosphoric acid and its salts precipitate yellow ammonium phosphomolybdate from an excess of a nitric acid solution of ammonium molybdate.

**Other Compounds of Phosphorus.** — **Phosphine** ($PH_3$) is analogous to ammonia ($NH_3$), though it is not alkaline. It

is made by heating sodium (or potassium) hydroxide with phosphorus. It is poisonous, and has a disagreeable odor; it usually takes fire spontaneously in the air owing to the presence of an inflammable compound of phosphorus and hydrogen. Phosphine itself does not take fire spontaneously. It combines with other substances, forming phosphonium compounds, which are analogous to ammonium compounds, *e.g.*: —

$$\underset{\text{Phosphine}}{PH_3} + \underset{\substack{\text{Hydriodic}\\\text{Acid}}}{HI} = \underset{\substack{\text{Phosphonium}\\\text{Iodide}}}{PH_4I}$$

**Phosphorus trichloride** ($PCl_3$) is a disagreeable smelling liquid, made by the combustion of dry chlorine and phosphorus; and **phosphorus pentachloride** ($PCl_5$) is a greenish solid made by passing chlorine into a vessel containing the trichloride. Both trichloride and pentachloride interact readily with water, forming phosphorus compounds and hydrochloric acid, thus: —

$$\underset{\substack{\text{Phosphorus}\\\text{Trichloride}}}{PCl_3} + \underset{\text{Water}}{3\,H_2O} = \underset{\substack{\text{Phosphorous}\\\text{Acid}}}{H_3PO_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid}}}{3\,HCl}$$

$$\underset{\substack{\text{Phosphorus}\\\text{Pentachloride}}}{PCl_5} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Phosphorus}\\\text{Oxychloride}}}{POCl_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid}}}{2\,HCl}$$

$$\underset{\substack{\text{Phosphorus}\\\text{Pentachloride}}}{PCl_5} + \underset{\text{Water}}{4\,H_2O} = \underset{\substack{\text{Phosphoric}\\\text{Acid}}}{H_3PO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid}}}{5\,HCl}$$

If either chloride is exposed to moist air, white fumes are formed owing to the liberation of hydrogen chloride (HCl).

When phosphorus pentachloride is heated, it sublimes without melting, and under special conditions of temperature and pressure it becomes a vapor. The molecular weight determined from the density of this vapor at about 300° C. is only about half the calculated value, *i.e.* 104 instead of 208.5. Examination of this vapor shows that it is

not phosphorus pentachloride, but almost entirely a mixture of phosphorus trichloride vapor and chlorine gas. The color is greenish and these two components can be separated by diffusion. These facts mean that phosphorus pentachloride when heated dissociates into phosphorus trichloride and chlorine. The reaction is reversible and the equation may be written thus: —

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

At 300° C. equilibrium is maintained by about 3 per cent of phosphorus pentachloride and 97 per cent of the trichloride and chlorine. This equilibrium may be displaced and the reaction sent in the reverse direction by increasing the concentration of one of the reaction products, *i.e.* by adding phosphorus trichloride or chlorine to the tube in which the equilibrium prevails. As a matter of fact, when phosphorus pentachloride is vaporized in a vessel containing an excess of the trichloride vapor, the dissociation of the pentachloride is reduced to a minimum, for the vapor density of the pentachloride then corresponds to a molecular weight of 209, the calculated value being 208.5.

**Matches.** — Phosphorus is chiefly used in the manufacture of matches. Soft wood is cut by machinery into the desired shape. The cards or sticks are fixed in a frame, and one end is first dipped into melted sulphur or paraffin and then into the phosphorus mixture. The latter consists usually of different proportions of phosphorus, manganese dioxide, glue, and a little coloring matter. Manganese dioxide may be replaced by other oxidizing agents. These matches are the ordinary friction or sulphur kind. By rubbing them on a rough surface enough heat is generated to cause the phosphorus to unite with the oxygen of the oxidizing agent, and the heat thereby produced sets fire to the sulphur or paraffin, and this in turn kindles the wood. Since these matches are poisonous and liable to take fire, their manufacture has been prohibited in some countries (*e.g.* Switzerland and the Netherlands). Safety matches, which replace them, contain no yellow phosphorus. The head of this kind is usually

a colored mixture of antimony sulphide, potassium chlorate, and glue, while the surface upon which the match must be rubbed to light is covered with a mixture of red phosphorus, glue, and powdered glass.

**Relation of Phosphorus to Life.** — Phosphorus is essential to the growth of plants and animals. Plants take phosphates from the soil and store up the phosphorus compounds, especially in the fruit and seeds. Animals eat this vegetable matter, assimilate the phosphorus compounds, and deposit them in the bones, brain, and nerve tissue. Bones contain about 80 per cent of calcium phosphate ($Ca_3(PO_4)_2$). Part of the combined phosphorus consumed by animals is rejected by them, and often finds its way back into the soil.

The constant removal of phosphates by plants would soon exhaust the soil. Hence phosphorus is restored to the soil in the form of natural or artificial **fertilizers**. Natural fertilizers are (1) stable refuse, which always contains some of the phosphates from the food originally fed to the animals; (2) guano, which is the dried phosphatic and nitrogenous excrement of the sea birds that once lived in vast numbers in Peru and Chili; and (3) phosphate slag, which is a phosphorus by-product obtained in manufacturing steel. Artificial fertilizers are made from phosphate rock. This occurs in large beds in South Carolina, Tennessee, and Florida, which yield about a million tons a year. It consists of the hardened remains of land and marine animals, and is mainly tricalcium phosphate ($Ca_3(PO_4)_2$). It is insoluble in water, and must be changed into the soluble primary calcium salt ($H_4Ca(PO_4)_2$) before it can be easily taken up by plants. This soluble salt is called "superphosphate of lime." When phosphate rock is treated with sulphuric acid, the changes involved may be written thus: —

$$\underset{\text{Tricalcium Phosphate}}{Ca_3(PO_4)_2} + 2\,H_2SO_4 = \underset{\text{"Superphosphate of Lime"}}{H_4Ca(PO_4)_2} + 2\,\underset{\text{Calcium Sulphate}}{CaSO_4}$$

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = \underset{\text{Phosphoric Acid}}{2\,H_3PO_4} + 3\,CaSO_4$$

$$Ca_3(PO_4)_2 + H_2SO_4 = \underset{\text{Dicalcium Phosphate}}{H_2Ca_2(PO_4)_2} + CaSO_4$$

The aim is to convert the crude phosphate rock into "superphosphate," but the three reactions usually occur. The product is ground, dried, and packed in bags for the market. On standing, it may undergo "reversion," *i.e.* the "superphosphate" and the phosphoric acid may form insoluble phosphates, thus making the fertilizer less valuable. Sometimes "superphosphate" is mixed with compounds of nitrogen and of potassium to produce a complete fertilizer.

## Arsenic

**Occurrence.** — Arsenic (As) is found free in nature, but it usually occurs combined with sulphur, a metal, or both. The common arsenic ores are realgar ($As_2S_2$), orpiment ($As_2S_3$), arsenic pyrites or mispickel (FeSAs). Arsenic trioxide or arsenolite ($As_2O_3$) is also found. Small quantities of arsenic occur in many ores.

**Preparation and Properties.** — Arsenic is prepared in the laboratory by reducing arsenious oxide with charcoal in a glass tube; the arsenic is volatile and is deposited as a dark ring on the colder part of the tube. The change is represented thus: —

$$\underset{\text{Arsenious Oxide}}{2\,As_2O_3} + \underset{\text{Carbon}}{6\,C} = \underset{\text{Arsenic}}{As_4} + \underset{\text{Carbon Monoxide}}{6\,CO}$$

On a large scale arsenic is extracted from its ores by the method just indicated or by roasting arsenic pyrites (FeSAs) in the absence of oxygen.

Arsenic is a brittle, steel-gray solid. A freshly broken piece has a metallic luster, which disappears slowly in a moist atmosphere. It tends to crystallize. The specific gravity varies from 5.62 to 5.96. Heated in the air, it volatilizes without melting, and the vapor has an odor like garlic. At about 180° C. it burns in the air with a bluish flame, forming white arsenious oxide ($As_2O_3$).

The vapor density of arsenic at about 650° C. corresponds to the molecular weight 300. Since the atomic weight is 75, the molecular formula of arsenic vapor is $As_4$ at this temperature. At about 1700° C. the formula is $As_2$.

Metallic arsenic has few uses, the main one being to harden the lead which is made into shot.

**Arsenious Oxide** or **Arsenic Trioxide**, $As_2O_3$ or $As_4O_6$, is the most important compound of arsenic, and is often called simply "arsenic" or "white arsenic." Small quantities are found free in nature. The commercial substance is obtained as a by-product in the roasting of ores containing arsenic. There are two common varieties, a white, granular powder and an amorphous, glasslike solid. It is an odorless white solid with a faint metallic taste; it dissolves only slightly in cold water, but is transformed readily by hot hydrochloric acid into soluble arsenic trichloride ($AsCl_3$). **Arsenic trioxide is a violent poison.** The antidote is fresh ferric hydroxide, which may be quickly made by adding ammonium hydroxide to a ferric salt, *e.g.* ferric chloride; the efficiency of the antidote depends upon the fact that the ferric hydroxide (formed by the interaction of ammonium hydroxide and ferric chloride) produces an insoluble compound with the arsenic solution. Small doses of arsenic trioxide (2 to 3 grains) are usually fatal, but by habitual use the system appropriates larger doses without ill effects. Workmen in arsenic factories often accidentally swallow with impunity

quantities which would ordinarily prove fatal. It is used to a limited extent in making pigments, in manufacturing glass and arsenic compounds, in calico printing, in preserving skins, and in preparing certain insect and vermin poisons.

At ordinary pressures arsenic trioxide sublimes without melting, and the commercial substance is purified by subliming the impure arsenic dust taken from the flues or chambers connected with ore furnaces. The vapor density at about 800° C. requires the formula $As_4O_6$, but at a very high temperature the formula is $As_2O_3$. The formula is also $As_4O_6$ according to the boiling-point method.

**Other Arsenic Compounds.** — The native mineral **orpiment** ($As_2S_3$) is used in making a yellow paint, and **realgar** ($As_2S_2$) a red paint. Arsenic forms acids analogous to the acids of phosphorus, though they are less important. **Orthoarsenic acid** ($H_3AsO_4$) is a white deliquescent solid prepared by the interaction of concentrated nitric acid and arsenic or arsenious oxide. **Arsenious acid** ($H_3AsO_3$) is known only in the solution of its corresponding anhydride ($As_2O_3$), resembling carbonic acid ($H_2CO_3$) in this respect. Several salts of the acids of arsenic are of interest. **Sodium arsenate** ($HNa_2AsO_4$) and **sodium arsenite** ($Na_3AsO_3$) are occasionally used in dyeing. Scheele's green is chiefly copper arsenite ($HCuAsO_3$), and was formerly used to make a cheap green paint and to color wall paper. The complex arsenic compound (copper aceto-arsenite) called **Paris green** is a light green powder; it is very poisonous and is used to exterminate potato bugs and other insects.

**Arsenic trisulphide**, $As_2S_3$, and **pentasulphide**, $As_2S_5$, are obtained as yellow precipitates by passing hydrogen sulphide gas into acid solutions of arsenious and arsenic compounds respectively. The formation of this yellow sulphide

is one **test for arsenic.** These sulphides form soluble sulpho-salts with alkaline sulphides, *e.g.*: —

$$\underset{\text{Arsenious Sulphide}}{As_2S_3} + 3\,\underset{\text{Ammonium Sulphide}}{(NH_4)_2S} = 2\,\underset{\text{Ammonium Sulpharsenite}}{(NH_4)_3AsS_3}$$

Sulpharsenates are formed with yellow ammonium sulphide, thus: —

$$As_2S_3 + 3\,(NH_4)_2S + S_2 = 2\,\underset{\text{Ammonium Sulpharsenate}}{(NH_4)_3AsS_4}$$

These sulpho-salts are decomposed by hydrochloric acid into hydrogen sulphide gas and the yellow sulphides of arsenic.

**Marsh's Test for Arsenic.** — Arsenic itself is not poisonous, but its compounds are among the most poisonous substances known. Fortunately, combined arsenic is easily detected by a simple method, called Marsh's test. An apparatus for generating hydrogen is provided with a hard glass horizontal delivery tube, narrowed in places and drawn to a point. Pure zinc, pure dilute sulphuric acid, and the arsenic solution are put in the generator. Hydrogen and gaseous hydrogen arsenide (or arsine ($AsH_3$)) are formed. If this mixture is lighted at the end of the delivery tube, it burns with a bluish flame, and metallic arsenic is deposited as a black metallic coating on cold porcelain held in the flame; or if the tube is heated in front of a narrow place, arsenic is deposited at this point. This deposit dissolves in sodium hypochlorite solution, but a deposit of antimony, similarly produced, does not dissolve. By this delicate test the merest trace of arsenic is readily and positively detected.

## Antimony

**Occurrence.** — Small quantities of free antimony are found. The most common ore is stibnite ($Sb_2S_3$), which occurs in China, Japan, Austria-Hungary, France, Algeria,

Italy, Mexico, and Turkey. Deposits in California and Nevada are also utilized.

Stibnite was found in the fifteenth century. The Latin name of antimony is *stibium*, from stibnite, which gives the symbol of the element, Sb.

**Preparation and Properties.** — Antimony is prepared industrially by two methods. In one the sulphide is roasted, and the oxide thus formed is reduced with charcoal. Equations representing the main changes are —

$$\underset{\text{Antimony Sulphide}}{Sb_2S_3} + \underset{\text{Oxygen}}{5\,O_2} = \underset{\text{Antimony Oxide}}{Sb_2O_4} + \underset{\text{Sulphur Dioxide}}{3\,SO_2}$$

$$Sb_2O_4 + 4\,C = 2\,Sb + 4\,CO$$

The other method consists in heating the sulphide with iron, the equation for the chemical change being —

$$\underset{\text{Antimony Sulphide}}{Sb_2S_3} + \underset{\text{Iron}}{3\,Fe} = \underset{\text{Antimony}}{2\,Sb} + \underset{\text{Iron Sulphide}}{3\,FeS}$$

Antimony is a silver-white, crystalline, brittle solid. Its specific gravity is 6.7. At ordinary temperatures antimony does not tarnish in the air, but when heated, it burns with a bluish flame, forming the white, powdery antimony trioxide ($Sb_2O_3$). The melting point is about 625° C. Powdered antimony burns brilliantly when added to chlorine, bromine, or iodine, owing to the vigorous and rapid combination with these elements. Nitric acid oxidizes it to $Sb_2O_3$ or to antimonic acid ($H_3SbO_4$), and *aqua regia* converts it into antimony trichloride ($SbCl_3$). It is one constituent of type metal (see Alloys of Lead) and other alloys.

**Compounds of Antimony.** — Antimony forms **stibine** ($SbH_3$), which is analogous to ammonia ($NH_3$) and arsine ($AsH_3$), pyro- and meta- acids, the **oxides**, $Sb_2O_3$, $Sb_2O_4$, $Sb_2O_5$,

and halogen compounds. It also forms complex compounds in which antimony acts as a metal. **Tartar emetic**, or potassium antimonyl tartrate ($KSbO \cdot C_4H_4O_6$), is a white solid, soluble in water; it is used as a medicine and as a mordant in dyeing cotton. (The group SbO is called antimonyl.) **Antimony trisulphide** ($Sb_2S_3$) as prepared in the laboratory is an orange red solid; it is formed by passing hydrogen sulphide gas into a solution of antimony — the **test for antimony**. The native sulphide, or **stibnite**, is a lustrous, blue-gray mineral, often beautifully crystallized. Antimony chloride ($SbCl_3$) is formed by the action of chlorine upon the metal or by boiling the metal in *aqua regia;* with water the trichloride forms a white solid called an oxychloride (SbOCl). The formation of **antimony oxychloride** is sometimes used as a test for antimony, but the more common test is the formation of the orange red sulphide ($Sb_2S_3$). The sulphides of antimony ($Sb_2S_3$ and $Sb_2S_5$) form salts with alkaline sulphides, which behave like the corresponding arsenic compounds.

## Bismuth

**Occurrence.** — Bismuth (Bi) is usually found in the native state, though it is not abundant nor widely distributed. The oxide ($Bi_2O_3$) or bismite, and the sulphide ($Bi_2S_3$) or bismuthinite, are the common ores. The world's supply comes from Saxony.

**Preparation and Properties.** — Bismuth is prepared from the native metal by melting it on an inclined plate and allowing it to drain away from the solid impurities. Sometimes the sulphide is roasted and the resulting oxide is reduced with charcoal, as in the case of antimony.

Bismuth is a gray-white metal with a red tinge. Like antimony, it is hard and brittle. It does not tarnish in dry

air, but it grows dull in moist air; and when heated in air it burns with a bluish flame, forming the yellowish oxide ($Bi_2O_3$). Its specific gravity is about 9.74. Hydrochloric acid does not readily attack it; but nitric acid converts it into a nitrate, hot sulphuric acid into a sulphate, and *aqua regia* into a chloride.

Bismuth melts at about 270° C. But a mixture of bismuth, lead, and tin melts at a low temperature. For example, Newton's metal melts at 95° C. and Rose's metal at 100° C.; while Wood's metal, which contains cadmium, melts at only 66°–71° C. These metallic mixtures are called **fusible metals** or **alloys**. They are used in making casts of wood cuts; but more often as safety plugs in steam boilers to prevent explosions, as a fuse in electrical apparatus to prevent a short circuit, and as a link to hold in place fireproof doors and the valves in the automatic sprinkling apparatus now installed in large buildings.

**Compounds of Bismuth.** — Bismuth forms no compounds with hydrogen. There are four oxides, but only two are well known. **Bismuth trioxide** ($Bi_2O_3$) is a pale yellow powder, and the **pentoxide** ($Bi_2O_5$) is a brown powder. Bismuth trioxide is used to fix the gilding on porcelain. The **trichloride** ($BiCl_3$) is formed by the action of chlorine upon bismuth, or by treating bismuth with *aqua regia*. With an excess of water the trichloride forms the **oxychloride** (BiOCl), which is a pearl-white powder insoluble in water. The formation of the oxychloride is the usual **test for bismuth.** Bismuth, being a metal, forms hydroxides ($Bi(OH)_3$ and BiO . OH). Normal bismuth nitrate ($Bi(NO_3)_3$) when treated with hot water forms basic bismuth nitrate ($Bi(OH)_2NO_3$ or $BiONO_3$). The latter, often called **subnitrate of bismuth**, is a white powder, and is used as a medicine for dyspepsia and as a cosmetic.

**The Nitrogen Family.** — This family illustrates typically the relation of atomic weight to properties, for these elements display a gradual change from non-metal to metal as we pass from nitrogen (atomic weight 14.01) through the periodic members to bismuth (atomic weight 208.0). Nitrogen and phosphorus are distinctly non-metallic, arsenic is both non-metallic and metallic, antimony is increasingly metallic, while bismuth is a typical metal. They form analogous compounds, for example: —

| | | | |
|---|---|---|---|
| $NH_3$ | $N_2O_3$ | $N_2O_5$ | —— |
| $PH_3$ | $P_2O_3$ | $P_2O_5$ | $PCl_3$ |
| $AsH_3$ | $As_2O_3$ | $As_2O_5$ | $AsCl_3$ |
| $SbH_3$ | $Sb_2O_3$ | $Sb_2O_5$ | $SbCl_3$ |
| —— | $Bi_2O_3$ | $Bi_2O_5$ | $BiCl_3$ |

### Problems and Exercises

1. Calculate the percentage composition of (*a*) sodium phosphate ($Na_3PO_4$), (*b*) dihydrogen sodium phosphate ($H_2NaPO_4$), (*c*) disodium phosphate ($HNa_2PO_4$), (*d*) microcosmic salt ($HNaNH_4PO_4$).

2. How much phosphorus is needed to remove the oxygen from a liter of air? (Assume (1) $2\,P + 5\,O = P_2O_5$, and (2) air is 20 per cent oxygen.)

3. How much phosphorus is there in a ton (2000 lb.) of bone ash if 70 per cent of the sample is calcium phosphate ($Ca_3(PO_4)_2$)?

4. If a skeleton weighs 25 lb. and contains 60 per cent calcium phosphate, how much phosphorus does it contain?

5. What is the weight of a cylindrical stick of ordinary phosphorus 10 cm. long and 15 mm. in diameter? (Suggestion. — What is the specific gravity of phosphorus?)

6. Calculate the percentage composition of (*a*) orpiment ($As_2S_3$), (*b*) realgar ($As_2S_2$), (*c*) white arsenic ($As_2O_3$).

7. What is the weight of a piece of antimony 25 cm. long, 15 cm. wide, and 2 mm. thick?

8. What volume of chlorine and of phosphorus trichloride is formed by the complete dissociation of 20 l. of phosphorus pentachloride?

9. If 18.5854 gm. of phosphorus yield 42.584 gm. of phosphorus

pentoxide, what is the atomic weight of phosphorus? (At. wt. of oxygen = 16.)

10. If 2.99091 gm. of antimony combine with 1.19495 gm. of sulphur to form antimony sulphide ($Sb_2S_3$), what is the atomic weight of antimony if the atomic weight of sulphur is 32.07?

11. Suppose 29.5305 gm. of bismuth trioxide ($Bi_2O_3$) yield 3.044 gm. of oxygen. If 16 is the atomic weight of oxygen, what is the atomic weight of bismuth?

12. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): (*a*) Arsenious chloride, arsenic chloride, hydrogen arsenide, arsenic iodide; (*b*) hydrogen antimonide, antimonic chloride, antimonious sulphide; (*c*) bismuth hydroxide, bismuth nitrate, bismuth sulphate; (*d*) calcium phosphide, acid calcium phosphate, phosphorous bromide, phosphoric iodide, magnesium phosphate (ortho), ammonium magnesium phosphate.

## CHAPTER XXIV

### Metals and Metallurgy

**Introduction.** — The elements studied thus far are chiefly non-metals. Metals, however, have been mentioned, and many of their properties have been discussed. In the present chapter we shall review these properties and prepare the way for a fuller treatment of the metals.

**Metals and Non-metals.** — Many years ago the chemical elements were divided into two classes, called metals and non-metals. The division was based largely on the conspicuous physical properties of the elements. The opaque, lustrous, more or less heavy, hard, ductile, malleable, tenacious solids were called **metals**. All gases and certain solids, such as carbon, sulphur, phosphorus, and iodine, were called **non-metals**. Their chemical properties do not permit such a sharp dividing line, however, to be drawn between metals and non-metals. Some elements have pronounced properties, like the non-metal sulphur and the metal iron; these are typical. A few elements have variable properties; sometimes they act as metals and sometimes as non-metals. Antimony and arsenic belong to this border-line class; they are occasionally called the **metalloids**. The classification into metals and non-metals is not accurate from a strictly chemical standpoint, but it is serviceable. The use in common life of the words *metallic* and *metal* seldom leads to confusion.

Although lists of the metals and non-metals have already been given, a repetition on a slightly different basis is not inappropriate in this chapter. The following is a

TABLE OF IMPORTANT METALS, METALLOIDS, AND NON-METALS

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Metals | Sodium<br>Potassium<br>—<br>Copper<br>Silver<br>Gold | Calcium<br>Strontium<br>Barium<br>—<br>Magnesium<br>Zinc<br>Cadmium<br>Mercury | Aluminium | Tin<br>Lead | Antimony<br>Bismuth | Chromium | Manganese | Iron<br>Cobalt<br>Nickel<br>—<br>Platinum |
| Non-metals | Hydrogen | | Boron | Carbon<br>Silicon | Nitrogen<br>Phosphorus<br>Arsenic | Oxygen<br>Sulphur | Fluorine<br>Chlorine<br>Bromine<br>Iodine | |
| Metalloids | | | Aluminium | Tin | Antimony<br>Arsenic | Chromium | Manganese | |

**Physical Properties of Metals.** — The physical properties of most metals are familiar. The properties of individual metals vary somewhat, depending upon the method of manufacture and the temperature. Until recently some metals were known only as powders, but the electrothermal and aluminothermal processes now enable us to prepare most of them in coherent masses. All metals have a **metallic luster**, *i.e.* the marked property of reflecting light from their polished or untarnished surfaces. All are **opaque** except in very thin films. The **color** of many is white, though the tint varies. Thus, in a compact state silver, sodium, aluminium, mercury, magnesium, iron, and tin are nearly pure white, while bismuth is reddish white and potassium is bluish. Copper is the only red metal and gold the only yellow one which is an element. When powdered, several metals are dark, some even black. Most metals are **malleable** and **ductile**, *i.e.* they can be hammered or rolled into sheets and drawn into wire. Gold, copper, silver, iron, platinum, and aluminium possess both these properties to a marked degree; while lead, tin, and zinc are very malleable though not especially ductile. Antimony and bismuth are brittle. The **hardness** of metals varies. At the ordinary temperature mercury is a liquid, sodium and lead can be cut easily with a knife, and so on through the list up to iridium, which is as hard as steel. In **specific gravity**, which was once thought to be very high, the metals range between lithium, which has the specific gravity .534, and osmium, which has the specific gravity 22.48. Sodium and potassium are lighter than water, while magnesium has the specific gravity 1.75, and aluminium 2.58. Metals **conduct heat and electricity**. They also vary in this property. Silver, copper, and aluminium are the best conductors, and have therefore many practical applications. Bismuth is the poorest conductor.

**Chemical Properties of Metals.** — Bases are formed when oxides of metals dissolve in water. On the other hand acids result from dissolving oxides of non-metals. Thus: —

| | | | | |
|---|---|---|---|---|
| $CaO$ | + | $H_2O$ | = | $Ca(OH)_2$ |
| Calcium Oxide | | | | Calcium Hydroxide |
| $SO_3$ | + | $H_2O$ | = | $H_2SO_4$ |
| Sulphur Trioxide | | | | Sulphuric Acid |

Metals, therefore, are base-forming elements. When compounds of metals are dissolved in water, the metal becomes the positive ion or cation, and the solutions have properties characteristic of the metal in the ionic state. Thus, solutions of copper nitrate and copper sulphate respond to the same test for copper because both contain copper ions ($Cu^{++}$). Sometimes the solution contains the metal as part of a compound ion, *e.g.* in solutions of potassium ferrocyanide the iron is present as the ion $Fe(CN)_6^{----}$.

**Occurrence of Metals.** — Only a few metals are found uncombined or free in the earth's crust, and these are seldom pure. Of the six metals known to the ancients (gold, copper, silver, tin, iron, and lead) all except tin and lead are found free. The metals which occur free in the earth's crust are called **native**, while their compounds are called **minerals**; the term *mineral*, however, is also applied to certain inorganic substances found in the earth's crust (*e.g.* sulphur, graphite, silica). Those minerals from which metals can be profitably extracted are called **ores**; sometimes the term *ore* is also applied to a rock containing native metals, *e.g.* gold ore or copper ore. The most abundant classes of ores are oxides, sulphides, carbonates, sulphates, and hydroxides. Many ores contain arsenic. Some ores are very complex.

**Preparation of Metals.** — The series of operations by which useful metals are extracted from their ores is called **metallurgy**. It includes preliminary treatment, smelting, electrolysis, refining, and other necessary operations.

The object of the **preliminary treatment** is to prepare the ore for smelting or for a similar operation. The ore as it comes from the mine is usually mixed with earthy matter or rock called **gangue**. This impurity is removed by mechanical or chemical processes, sometimes by both. The mechanical process illustrates one kind of preliminary treatment. The ore is first crushed in a stamp mill. This is a huge, heavy mortar and pestle. The pestle falls repeatedly upon the ore, which is slowly fed into the mortar or die. A current of water (or air) forces the fine particles out of the mortar through a sieve. The lighter particles of the impurities are washed away, and the metallic grains are extracted by another mechanical operation, though chemical processes are frequently employed, especially with inferior ores. This separation of the valuable part of the ore from the gangue and reducing it to a smaller bulk is often called **ore dressing** or **concentration**. Copper is extracted from Lake Superior ores mainly by this method of preliminary treatment.

Gold and silver ores are often treated like copper and then extracted from the slime by mercury. The latter operation is called **amalgamation**. The most common method of extracting metals from their ores is by **smelting**. The process varies with the kind and composition of the ore. Essentially, it consists in heating a mixture of the ore and coke (or coal) in a furnace. The ores used must, as a rule, be oxides. Sulphides, hydroxides, and carbonates are first roasted or calcined to convert them into oxides. The essential chemical change in smelting is a reduction of the oxide by carbon. The carbon and oxygen unite and pass off

as a gas, leaving the molten metal at the bottom of the furnace. Limestone or a similar substance is often added to the mixture as a **flux**, *i.e.* to facilitate the melting and to assist in removing the impurities as a glassy substance, called **slag**. The operation is conducted in different kinds of furnaces. Iron, for example, is melted in a huge upright furnace called a blast furnace (Fig. 80), because a current of air is forced through the melted mass to facilitate the fusion and chemical changes. In such a furnace the fuel and ore are in direct contact. When this is undesirable, the reverberatory furnace is used (Fig. 64). As the figure shows, in this furnace the flame is reflected or reverberated upon the ore under treatment. In this kind of furnace the ore may be oxidized or reduced without coming in contact with the fuel. Some ores demand special methods, which will be described in connection with the metals.

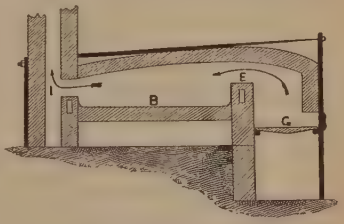



FIG. 64. — Reverberatory furnace. The fire burns on the grate *G* and the long flame which passes over the bridge *E* is reflected down by the sloping roof upon the contents of the furnace. Gases escape through *I*. The charge, which rests upon the bed *B*, does not come in contact with the fuel, but is oxidized or reduced by the flame.

Electrolysis is used to extract some metals, especially aluminium and magnesium. Other metals, notably copper, are purified by electrolysis. A few metals are extracted by a wet process. That is, the ores are dissolved, and the metal is then precipitated by adding some substance or by electrolysis. Thus, inferior gold ores are dissolved by treatment with potassium (or sodium) cyanide, and the gold is then precipitated by zinc.

Some metals, hitherto rare, are obtained by reducing their

oxides with carbon in the electric furnace or by heating the powdered oxide with aluminium.

**Alloys** are mixtures or compounds of two or more metals. Some fused metals mix in all proportions, while others seem to form definite compounds. The properties of alloys vary with the constituents and their proportions. Some alloys, especially those of copper and of lead, have many industrial uses. Alloys in which mercury is a constituent are called **amalgams.**

### Problems

1. What is the specific gravity of gold, if a piece weighs 4.676 gm. in air, and loses 0.244 gm. when weighed in water? (Note. — Specific gravity equals the weight in air divided by the loss of weight in water.)

2. A piece of aluminium weighs 150 gm. in air, and 75 gm. in water. What is its specific gravity?

3. A piece of iron weighs 292.8 gm. in air and 255.3 gm. in water. What is its specific gravity?

4. A piece of copper weighing 50 gm. in air lost 5.6 gm. when weighed in water. What is its specific gravity?

5. A piece of lead pipe weighs 158.9 gm. in air and 144.9 gm. in water. Calculate the specific gravity.

# CHAPTER XXV

## Sodium, Potassium, Lithium, and Ammonium — Spectrum Analysis

**Introduction.** — Sodium and potassium, together with the less common element lithium and the rare elements rubidium and cæsium, form a natural family in Group I of the periodic classification, known as alkali metals. These elements and their corresponding compounds resemble each other closely.

Compounds of the hypothetical metal ammonium are conveniently treated in this chapter because their chemical relations are similar.

Sodium and potassium were discovered by Sir Humphry Davy in 1807 by the electrolysis of their hydroxides. Bunsen, by means of the spectroscope, discovered lithium in 1855, cæsium in 1860, and rubidium in 1861.

### Sodium

**Occurrence.** — Sodium is not found free. Sodium chloride and sodium nitrate are the most abundant compounds. Many minerals, rocks, marine plants, and mineral waters contain combined sodium. About 2.5 per cent of the earth's crust is sodium.

The symbol of sodium, Na, is from the Latin word *natrium*, which in turn comes from the Greek word *natron*, an old name of sodium carbonate.

**Preparation.** — Sodium is manufactured on a large scale by the electrolysis of fused sodium hydroxide. This method,

used on a small scale by Davy in 1807 to isolate sodium, became practicable only recently and is known as the Castner method. Figure 65 is a sketch of the apparatus. The body of the steel cylinder rests within a heated flue. The iron cathode ($C$) passes up through the bottom of the cylinder into the fused sodium hydroxide. A cylindrical collecting pot ($P$) terminating in a wire gauze ($G$, $G$) surrounds the cathode. Several carbon bars ($A$, $A$) dip into the vessel from above, and constitute the anode. As the electrolysis proceeds, sodium and hydrogen are liberated at the cathode and oxygen at the anode. The oxygen escapes through pipes (not shown in the sketch), while the sodium and hydrogen collect in $P$. The hydrogen escapes through the top of $P$, while the sodium, which is protected from the oxidizing action of the air by the hydrogen, is ladled out at intervals.

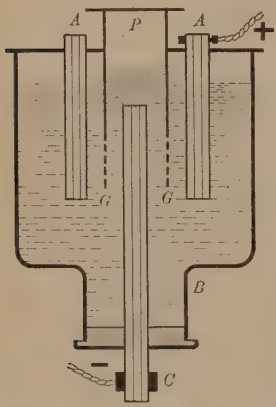



FIG. 65. — Apparatus for the manufacture of sodium by the electrolysis of sodium hydroxide.

**Properties.** — Sodium is a silver-white metal. It can be easily cut with a knife and molded with the fingers. It is light enough to float upon water, since its specific gravity is 0.9712 (at 20° C.). Heated in the air, it melts at about 96° C., and at a higher temperature it burns with a brilliant yellow flame, forming sodium peroxide ($Na_2O_2$). This intense yellow color is characteristic of sodium and is a **test for the element** (free or combined). In moist air the bright surface quickly tarnishes, and sodium as usually seen

has a yellow or gray-brown coating. It is, therefore, kept under kerosene or a liquid free from water.

It decomposes water at ordinary temperatures, liberating hydrogen and forming sodium hydroxide, thus: —

$$\underset{\text{Sodium}}{2\,Na} + \underset{\text{Water}}{2\,H_2O} = \underset{\text{Sodium Hydroxide}}{2\,NaOH} + \underset{\text{Hydrogen}}{H_2}$$

If held in one place upon water by filter paper, enough heat is generated to set fire to the hydrogen, which burns with a yellow flame, owing to the presence of volatilized sodium. If sodium is melted in chlorine, the two elements combine with a brilliant flame, forming sodium chloride. Davy, in 1810, proved in this way that common salt is really nothing but sodium chloride. It combines with hydrogen and forms a white solid called sodium hydride (NaH). If mixed with mercury, it forms sodium amalgam, which is sometimes used instead of sodium itself.

A molecule of sodium has been found to be monatomic by the vapor density and the freezing-point methods.

Sodium is **used** in the laboratory to extract water from alcohol and ether and to prepare organic compounds. Large quantities are consumed in the manufacture of sodium peroxide ($Na_2O_2$) and sodium cyanide (NaCN). Its power to reduce oxides gives it limited use in preparing certain rare metals, e.g. zirconium, tantalum, niobium, and thorium, though it is being replaced by aluminium. (See Thermit.)

**Sodium Chloride**, NaCl, is the most important compound of sodium. It is one of the most abundant substances, and is familiar under the name of **salt**, **common salt**, or table salt. The presence of salt in the ocean, in lakes and springs, and in the soil is mentioned in the oldest historical records. Sodium chloride constitutes about 77 per cent

of the salts found in sea water and by far the largest part of the salt deposits in the earth's crust.

**Preparation of Salt.** — The chief sources of salt are sea water, rock salt deposits, and brines. (1) In warm countries, as on the shores of the Mediterranean Sea, shallow ponds of sea water near the shore are evaporated by exposure to the sun and wind, and the salt is collected. In some regions sea water is first concentrated by allowing it to trickle over heaps of brush and then evaporate to crystallization in shallow pans. In cold countries, as on the shores of the White Sea in Russia, sea water is allowed to freeze and the ice is removed. The ice contains no salt, so the operation is repeated until the remaining liquid becomes concentrated enough to evaporate profitably over a fire. (2) Deposits of salt are found in many parts of the globe, the most important being in England, Austria-Hungary, and Germany. In these regions and some parts of the United States the salt is mined and purified like other minerals. This variety is coarse and often impure, and is largely used in curing meat and preserving hides. (3) Most of the salt produced in the United States is obtained from natural or artificial brines, *i.e.* from concentrated solutions of salt. Artificial brines are made by forcing water into salt deposits. Brines are obtained in New York, Michigan, Kansas, Ohio, West Virginia, California, Utah, and Louisiana. They are evaporated in vats by the sun's heat or by heating in kettles or pans.

All these methods give a product containing as impurities salts of calcium and magnesium, which are largely removed by further special treatment. According to the standard established by the United States Department of Agriculture, dry table or dairy salt must not contain over 1.4 per cent of calcium sulphate, .5 per cent of calcium and magnesium chlorides, and .1 per cent of matter insoluble in water. The dampness of salt is due to traces of magnesium and calcium chlorides. (See Deliquescence.)

**Properties and Uses of Salt.** — Salt is rather soluble in water, 100 gm. of water dissolving about 36 gm. of salt at 0° C. and 40 gm. at 100° C. It crystallizes in cubes, which often snap open sharply (*i.e.* decrepitate) when heated, owing to the sudden vaporization of the inclosed water. This substance is an essential ingredient of the food of man and animals. Besides its universal domestic use, enormous

quantities are consumed in the preparation of many sodium and chlorine compounds, especially sodium carbonate, hydrochloric acid, and bleaching powder.

**Sodium Carbonate**, $Na_2CO_3$, is next to sodium chloride in importance. Small quantities of hydrated sodium carbonates are found in Egypt, Russia, and in California and Nevada. Formerly it was obtained from the ashes of marine plants, but sodium chloride is now the source. The manufacture of sodium carbonate is one of the most extensive chemical industries. Two processes are used, the Leblanc and the Solvay.

The **Leblanc Process** has three stages. (1) Sodium chloride is changed into sodium sulphate by sulphuric acid, the equation for the change being —

$$\underset{\text{Sodium Chloride}}{2\,NaCl} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Hydrochloric Acid}}{2\,HCl}$$

This operation is called the salt cake process; the impure product, called "salt cake," contains about 95 per cent of sodium sulphate. The hydrochloric acid is a profitable by-product. (See Hydrochloric Acid.) (2) and (3) The sodium sulphate is reduced to sodium sulphide by heating the "salt cake" with coal; and the resulting sodium sulphide is changed into sodium carbonate by heating with limestone. These two chemical changes, which are accomplished by one operation, are represented by the following equations: —

$$\underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Carbon}}{2\,C} = \underset{\text{Sodium Sulphide}}{Na_2S} + \underset{\text{Carbon Dioxide}}{2\,CO_2}$$

$$\underset{\text{Sodium Sulphide}}{Na_2S} + \underset{\text{Limestone}}{CaCO_3} = \underset{\text{Sodium Carbonate}}{Na_2CO_3} + \underset{\text{Calcium Sulphide}}{CaS}$$

This operation is called the black ash process. The product is a dark brown or gray porous mass, and contains, besides 37 to 45 per cent of sodium carbonate, considerable calcium sulphide and other impurities. The sodium carbonate is rapidly separated from the insoluble portions of the "black ash" by extraction with a regulated

stream of water. The concentrated solution of sodium carbonate thus obtained is evaporated to crystallization, and the crude crystals are ignited. This product is known as soda ash, and from its solution in water are obtained soda crystals or sal soda ($Na_2CO_3 . 10\,H_2O$).

The **Solvay Process**, often called the ammonia-soda process, consists in saturating a cold concentrated solution of sodium chloride first with ammonia gas and then with carbon dioxide gas. The equation for the complete chemical change is —

| $H_2O$ | + | $NaCl$ | + | $NH_3$ | + | $CO_2$ | = | $HNaCO_3$ | + | $NH_4Cl$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Water | | Sodium Chloride | | Ammonia | | Carbon Dioxide | | Acid Sodium Carbonate | | Ammonium Chloride |

The acid sodium carbonate is nearly insoluble in the cold ammonium chloride solution, and therefore separates. It is changed, by heating, into sodium carbonate, thus: —

| $2\,HNaCO_3$ | = | $Na_2CO_3$ | + | $CO_2$ | + | $H_2O$ |
|---|---|---|---|---|---|---|
| Acid Sodium Carbonate | | Sodium Carbonate | | Carbon Dioxide | | Water |

The liberated carbon dioxide is used again, and from the ammonium chloride the ammonia is also recovered and used.

**Properties and Uses of Sodium Carbonate.** — Crystallized sodium carbonate ($Na_2CO_3 . 10\,H_2O$) is often called alkali or **soda.** It loses water in the air, becoming dull at first and finally falling to a powder, owing to the fact that its vapor pressure is greater than the average vapor pressure of the air; this phenomenon, as already stated, is called efflorescence. When heated, it melts in its water of crystallization, and continued heating changes it into a white anhydrous salt ($Na_2CO_3$). It is readily soluble in water, and the solution, which is strongly alkaline, is widely used as a cleansing agent, hence the name **washing soda.** A water solution of sodium carbonate is alkaline owing to hydrolysis. Sodium carbonate ionizes into $2\,Na^+$ and $CO_3^{--}$, but the $CO_3$-ions are unstable and form $HCO_3$-ions with the H-ions from the slightly dissociated water; this removal of H-ions finally leaves in the solution sufficient OH-ions to produce an alkaline reaction to litmus.

Besides its general use as a cleansing agent, enormous quantities of sodium carbonate are consumed in the glass and soap industries and in preparing sodium compounds.

**Sodium Bicarbonate**, $HNaCO_3$, is formed at one stage of the Solvay process (see above). It may also be prepared by treating crystallized sodium carbonate with carbon dioxide gas. It is a white solid, and is less soluble in water than the normal carbonate. When heated or when mixed with an acid or an acid salt, sodium bicarbonate gives up carbon dioxide. This property early led to its use in cooking, and gave the names **cooking soda, baking soda**, or simply soda.

Sodium bicarbonate is so called because in it the ratio of the $CO_3$ to the Na is twice that in the normal carbonate ($Na_2CO_3$). Although called acid sodium carbonate, a solution of the pure salt is practically neutral, the ions being $Na^+$ and $HCO_3^-$.

Sodium bicarbonate is one ingredient of baking powder and of various mixtures (except yeast) used to raise bread, cake, and other food. The other essential ingredient is cream of tartar (acid potassium tartrate), which has a mild acid reaction and thus liberates carbon dioxide from the sodium bicarbonate. Sour milk, which contains lactic acid, is sometimes used in place of cream of tartar. When pastry is raised with baking soda and cream of tartar, the escaping carbon dioxide puffs up the dough. Hence baking soda is often called **saleratus** — the salt which aerates (from the Latin words *sal*, salt, and *aer*, air or gas). Effervescing powders, such as Seidlitz powder, are mixtures of sodium bicarbonate and tartaric acid or one of its acid salts. When the ingredients are put into water, carbon dioxide is liberated. Sodium bicarbonate is used as a medicine to neutralize an acid stomach. For example, the

"soda mints" sometimes taken for this purpose are mainly sodium bicarbonate.

**Sodium Hydroxide** or **Caustic Soda**, NaOH, is a white deliquescent, corrosive solid. It absorbs water and carbon dioxide rapidly from the air. When exposed to the air, it becomes moist at first, then forms a concentrated solution, and ultimately solidifies, owing to transformation into sodium carbonate. The deliquescence of sodium hydroxide, as already stated, is due to the fact that its ready solubility produces a solution on the surface which has a lower vapor tension than the vapor pressure of the water vapor in the air; hence the solid continues to dissolve in the absorbed water until a solution is produced whose vapor tension equals the pressure of the water vapor in the surrounding air. It dissolves readily in water with rise of temperature, and the solution is strongly alkaline owing to the high degree of ionization of the solute. When heated, it melts easily, and is often cast into sticks for use in the laboratory.

Immense quantities are used in making hard soap, paper, and dyestuffs; in bleaching, and in refining kerosene oil.

Sodium hydroxide is manufactured by two general methods, one electrolytic and the other purely chemical. In the electrolytic method the sodium liberated from sodium chloride interacts with water and forms sodium hydroxide.

The apparatus used in one electrolytic process is shown in Figure 66. The graphite rods (*A*, *A*) serve as the anode and pass into the outer compartments into which a solution of sodium chloride slowly flows; the iron cathode (*C*) dips into the middle compartment from which the sodium hydroxide overflows. When the current passes, the chlorine ions migrate to the anode, where they lose their electric charges, become elementary chlorine, and escape through pipes (not shown); the sodium ions lose their charges upon the mercury

(*M*) which covers the floor of the cell, and thereby form an amalgam. By rocking the apparatus on the device *B*, *B*, the sodium amalgam flows beneath the partitions into the compartment *D*. Here the sodium is liberated as ions,

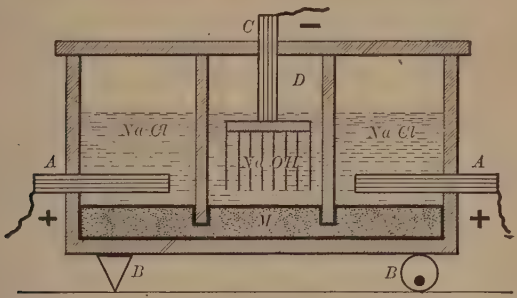



FIG. 66. — Apparatus for the manufacture of sodium hydroxide by the electrolysis of sodium chloride.

which migrate to the cathode, where they lose their charges. The elementary sodium reacts with the water, forming hydrogen (which escapes through pipes — not shown) and sodium hydroxide. The alkaline solution overflows into a special tank, and is evaporated to dryness.

The chlorine evolved in this process is liquefied, or utilized in the manufacture of bleaching powder and other chlorine compounds.

Sodium hydroxide was manufactured for many years by adding lime to a boiling, dilute solution of sodium carbonate, but this process has been almost entirely superseded by the electrolytic process. The essential chemical change is represented thus : —

| $Ca(OH)_2$ | + | $Na_2CO_3$ | = | $2\,NaOH$ | + | $CaCO_3$ |
|---|---|---|---|---|---|---|
| Calcium Hydroxide | | Sodium Carbonate | | Sodium Hydroxide | | Calcium Carbonate |

The solution of sodium hydroxide is separated from the insoluble calcium carbonate, and concentrated by heating in iron kettles to the desired strength.

**Sodium Sulphate**, $Na_2SO_4$, is one of the products obtained in the manufacture of sodium carbonate and of nitric acid (see above). At Stassfurt sodium sulphate is prepared by cooling to about 0° C. a mixture of magnesium sulphate and sodium chloride solutions; the equation is —

$$\underset{\text{Magnesium Sulphate}}{MgSO_4} + 2\,\underset{\text{Sodium Chloride}}{NaCl} = \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Magnesium Chloride}}{MgCl_2}$$

Sodium sulphate is a white solid. It dissolves readily in water, and when a concentrated solution made at 30° C. is cooled, large transparent crystals separate. They have the formula $Na_2SO_4.10\,H_2O$ and are called **Glauber's salt** from the discoverer. They lose water when exposed to air, and the salt continues to effloresce until it becomes an anhydrous powder. The crude salt is used in the glass and dyeing industries, and the purified salt as a medicine.

**Sodium Sulphite**, $Na_2SO_3$, is a white solid prepared by passing sulphur dioxide into sodium hydroxide solution. The crystallized salt has the formula $Na_2SO_3.7\,H_2O$. It interacts with sulphuric acid as follows: —

$$\underset{\text{Sodium Sulphite}}{Na_2SO_3} + H_2SO_4 = \underset{\text{Sodium Sulphate}}{Na_2SO_4} + \underset{\text{Sulphur Dioxide}}{SO_2} + H_2O$$

It is used as a source of sulphur dioxide and also as a preservative.

**Sodium Nitrate**, $NaNO_3$, is abundant in Chili, and is often called Chili saltpeter. It is a white solid, very soluble in water, especially hot water, and is slightly deliquescent. Large quantities are used as a fertilizer (either alone or mixed with compounds of potassium and of phosphorus) and for making nitric acid and potassium nitrate.

The natural deposits of sodium nitrate are in a dry region near the coast and cover over 200,000 acres. Chili controls the industry, and exports annually over a million tons. The crude salt, which looks like rock salt, is purified by crystallization into a product containing 94–98 per cent of the nitrate. The final mother liquid is a source of iodine. (See Iodine.)

**Sodium Nitrite**, $NaNO_2$, is a white solid. It is prepared by reducing sodium nitrate with lead, thus: —

| $NaNO_3$ | + | Pb | = | $NaNO_2$ | + | PbO |
|---|---|---|---|---|---|---|
| Sodium Nitrate | | Lead | | Sodium Nitrite | | Lead Oxide |

It liberates the oxides of nitrogen (NO and $NO_2$) upon the addition of sulphuric acid, and is used extensively in manufacturing dyes.

**Sodium Dioxide** or **Peroxide**, $Na_2O_2$, is a yellowish solid. It is used to bleach straw and delicate fabrics, and is an oxidizing agent. A fused form is sold as "oxone." With water it liberates oxygen, according to the equation —

$$\underset{\text{Sodium Dioxide}}{2\,Na_2O_2} + 2\,H_2O = \underset{\text{Oxygen}}{O_2} + \underset{\text{Sodium Hydroxide}}{4\,NaOH}$$

**Miscellaneous.** — As stated above, sodium compounds impart an intense yellow color to a Bunsen flame. Most sodium compounds dissolve in water and they yield a colorless cation ($Na^+$). The atomic weight of sodium is 23.00 and its valence is one.

**Sodium cyanide** (NaCN) is used to extract gold from poor ores. The sodium phosphates, sodium thiosulphate, acid sodium sulphite, sodium silicate, and sodium tetraborate or borax have already been described.

## Potassium

**Occurrence.** — This metal is not found free, but its compounds are abundant. The common minerals mica and feldspar are silicates containing potassium. By the decay of these and other minerals potassium compounds find their way into the soil, thence into plants and animals. Potassium salts are found in wood ashes, in suint (the oily substance washed from sheep's wool), in beet-sugar residues, and in the deposits in wine casks. Sea water and mineral waters contain potassium salts, particularly potassium chloride and potassium sulphate. Many potassium salts are found at Stassfurt, and they are the source of most potassium compounds. About 2.5 per cent of the earth's crust is potassium.

The **Stassfurt deposits** of the salts of potassium, magnesium, calcium, and sodium are near Magdeburg, Germany. The deposits are about five thousand feet thick and contain many salts which were deposited ages ago in beds or layers during the slow evaporation of an inclosed branch of the sea. The lowest bed is an enormous mass of more or less impure sodium chloride (called in this case rock salt or halite), which was deposited first. Upon this rest more or less regular layers of potassium and magnesium salts, higher still are calcium salts and at the top is a thick bed of sandstone. The different minerals are mined separately as far as possible and then separated into commercial products by an elaborate system of solution, evaporation, and crystallization. The most important Stassfurt potassium minerals are —

| | |
|---|---|
| Kainite . . . . . | $KCl, MgSO_4 . 3 H_2O$. |
| Carnallite . . . . . | $KCl, MgCl_2 . 6 H_2O$. |
| Polyhalite . . . . | $K_2SO_4, MgSO_4, 2 CaSO_4 . 2 H_2O$. |
| Sylvite . . . . . | $KCl$. |
| Picromerite . . . . | $K_2SO_4, MgSO_4 . 6 H_2O$. |

Many of the Stassfurt salts belong to a class of compounds called **double salts**, *i.e.* crystalline compounds of two or more normal salts with one another. Carnallite is a double

salt, and its formula is often written to emphasize this fact, thus KCl, $MgCl_2 . 6 H_2O$ instead of $KMgCl_3 . 6 H_2O$. Dilute aqueous solutions of double salts contain ions of the separate salts and exhibit no reactions which indicate combination of ions. There are other double salts. (See Alums.)

**Preparation.** — Potassium is prepared by the electrolysis of fused potassium chloride. Formerly it was manufactured by heating to a high temperature a mixture of potassium carbonate and carbon, or of potassium hydroxide and iron carbide.

**Properties.** — Like sodium, potassium is a soft, silver-white metal; it is light enough to float upon water — the specific gravity being .8621 (at 20° C.). Its brilliant luster soon disappears in air, owing to rapid oxidation. Potassium as ordinarily seen is covered with a grayish coating, and like sodium must be kept under mineral oil. It melts at 62.5° C., and at a higher temperature burns with a violet-colored flame. This color is characteristic of burning potassium, and is a **test for the metal** and its compounds. Like sodium, it decomposes water at ordinary temperatures, though more energetically. The reaction corresponds to the equation —

$$\underset{\text{Potassium}}{2\,K} + \underset{\text{Water}}{2\,H_2O} = \underset{\substack{\text{Potassium}\\\text{Hydroxide}}}{2\,KOH} + \underset{\text{Hydrogen}}{H_2}$$

The heat evolved immediately ignites the liberated hydrogen, and the melted potassium, surrounded by a violet flame, dashes to and fro upon the cold water. Potassium combines with the halogens and other elements more vigorously than sodium, and forms analogous compounds.

**Potassium Chloride**, KCl, is found native as sylvite in the Stassfurt deposits. It is also obtained in large quantities by heating a concentrated solution of carnallite

($KCl, MgCl_2 . 6\ H_2O$) and allowing potassium chloride to crystallize out from the cool solution. It is a white solid which crystallizes in cubes and otherwise resembles sodium chloride. It is used chiefly to prepare other potassium salts, especially the nitrate, hydroxide, carbonate, and chlorate.

Potassium bromide and iodide, which are analogous to the chloride, have been described (see these compounds).

**Potassium Nitrate**, $KNO_3$, is also called niter and saltpeter. It is formed in the soil near large cities in India and Persia by the decomposition of nitrogenous organic matter in the presence of potassium salts. (See Nitrification.) It is manufactured by mixing hot, concentrated solutions of native sodium nitrate and potassium chloride, which interact thus: —

| $NaNO_3$ | + | $KCl$ | = | $KNO_3$ | + | $NaCl$ |
|---|---|---|---|---|---|---|
| Sodium Nitrate | | Potassium Chloride | | Potassium Nitrate | | Sodium Chloride |

The sodium chloride, being the less soluble of the two, precipitates as the solution cools, and is removed. By further evaporation the potassium nitrate (together with a little sodium chloride) crystallizes out as "niter meal."

Potassium nitrate is a white solid. It dissolves only to a slight extent in cold water, but very freely in hot water. It is not deliquescent. If a solution is cooled slowly, large prismatic crystals are formed which do not contain water of crystallization. Such crystals have cavities in which there is impure water; this water cannot be removed by drying the crystals. When heated, these crystals decrepitate like those of sodium chloride. The taste is salty and cooling. It melts at about 339° C., and on further heating changes into **potassium nitrite** ($KNO_2$) and oxygen. It is stable in the air at ordinary temperatures, but at a high temperature potassium nitrate gives up oxygen readily,

especially to charcoal, sulphur, and organic matter. This oxidizing power leads to its extensive use in making gunpowder, fireworks, and matches.

**Gunpowder** is a mixture of potassium nitrate, charcoal, and sulphur. The ingredients are first purified, pulverized, and thoroughly mixed. This mixture is pressed, while damp, into a thin sheet; and the press cake thus formed is broken into small grains, which are sorted by sieves. The grains are then smoothed or glazed by rolling them in a barrel, again sifted, and finally dried at a low temperature. The proportions differ with the use of the powder. Modern black powder contains about 75 per cent of potassium nitrate, 15 of charcoal, and 10 of sulphur. When gunpowder burns in a closed space, a large volume of gas is suddenly formed. So enormously is this gas expanded by the heat that in an open space it would fill several hundred times the space taken by the powder itself. The pressure exerted by this expanding gas is many tons to the square inch. It is this pressure which forces the charge from a gun and tears a rock to pieces. The chemical changes attending the explosion of confined gunpowder are complex, as may be seen by the following equation:—

$$16\,KNO_3 + 21\,C + 5\,S = 5\,K_2CO_3 + 13\,CO_2 + K_2SO_4 + 3\,CO + 2\,K_2S_2 + 8\,N_2$$

Potassium Nitrate — Carbon — Sulphur — Potassium Carbonate — Carbon Dioxide — Potassium Sulphate — Carbon Monoxide — Potassium Sulphide — Nitrogen

The equation for the explosion when unconfined is much simpler, thus:—

$$2\,KNO_3 + 3\,C + S = 3\,CO_2 + N_2 + K_2S$$

Gunpowder is being rapidly replaced by smokeless powders. (See Cellulose.)

**Potassium Chlorate**, $KClO_3$, is a white, crystalline, lustrous solid. It tastes like potassium nitrate. It melts at about 334° C., and at a high temperature decomposes into oxygen and potassium chloride as final products, thus:—

$$KClO_3 = KCl + 3\,O$$

Potassium Chlorate — Potassium Chloride — Oxygen

It is used to prepare oxygen, and in the manufacture of dyes, matches, and fireworks. In the form of "chlorate of potash tablets" it is used as a remedy for sore throat.

Potassium chlorate was formerly manufactured by passing chlorine into calcium hydroxide (milk of lime) and adding potassium chloride to the mixture. The simplest equations for the complex changes may be written thus: —

$$\underset{\text{Calcium Hydroxide}}{6\,Ca(OH)_2} + \underset{\text{Chlorine}}{6\,Cl_2} = \underset{\text{Calcium Chlorate}}{Ca(ClO_3)_2} + \underset{\text{Calcium Chloride}}{5\,CaCl_2} + 6\,H_2O$$

$$Ca(ClO_3)_2 + \underset{\text{Potassium Chloride}}{2\,KCl} = \underset{\text{Potassium Chlorate}}{2\,KClO_3} + CaCl_2$$

This salt is now made by the electrolysis of a hot, concentrated solution of potassium chloride. The chlorine evolved at the anode interacts with the potassium hydroxide formed (by secondary chemical action) at the cathode and produces potassium chlorate. The latter is obtained from the solution by crystallization.

**Potassium Carbonate**, $K_2CO_3$, is a white solid. It is very soluble in water and deliquesces when exposed to the air, becoming a thick liquid at first and finally a solid. The property of deliquescence is due to the fact that the vapor pressure of its saturated solution at ordinary temperatures is less than the average pressure of the water vapor in the air. The solid residue is potassium bicarbonate, which is formed by the slow absorption of carbon dioxide from the air. A solution of potassium carbonate has a marked alkaline reaction. (See Sodium Carbonate.) It was formerly prepared in large quantities by extracting wood ashes with water and evaporating the solution to dryness; this process is still employed in some localities. The crude salt thus obtained has long been called potash and a purer product

is known as pearlash. The term *potash* is also sometimes applied to potassium hydroxide (KOH) and to potassium oxide ($K_2O$). It is used in the manufacture of hard glass, soft soap, and potassium compounds.

Potassium carbonate is obtained to some extent from suint by igniting the greasy mass and extracting the potassium carbonate with water. Beet-sugar residues also furnish potassium carbonate. After the sugar has been obtained from the beet sirup, the molasses is changed by fermentation into alcohol, which is distilled off; the liquid residue is evaporated to dryness and ignited, and the potassium carbonate extracted with water. Potassium carbonate is prepared by igniting the crude cream of tartar collected from the deposits in wine casks, and for this reason it is sometimes called salt of tartar. All these sources emphasize the intimate relation of potassium compounds to vegetable and animal life. Much of the commercial potassium carbonate is now made from potassium chloride by the Leblanc process. Another process is used, principally in Germany, owing to the abundance of crude potassium salts at Stassfurt. It consists essentially in forcing carbon dioxide into a solution of potassium chloride containing suspended magnesium carbonate, decomposing the complex compound of potassium and magnesium ($MgCO_3 . HKCO_3 . 4 H_2O$) with steam, and evaporating the filtered solution of potassium carbonate.

The name *potassium* comes from the word *potash*. The symbol, K, is from *kalium*, the Latin equivalent of *kali*, which is derived from an Arabic term for an alkaline substance.

**Potassium Hydroxide** or **Caustic Potash**, KOH, is a white brittle solid, resembling sodium hydroxide. It absorbs water and carbon dioxide very readily; and if exposed to the air, it soon becomes a thick solution of potassium carbonate. Like sodium hydroxide, it dissolves in water with evolution of heat, forming a markedly alkaline, caustic solution. Besides its use in the laboratory, large quantities are consumed in making soft soap.

Potassium hydroxide was formerly made in the same way as sodium hydroxide, viz. by adding lime or milk of lime to

a boiling dilute solution of potassium carbonate, the equation for the change being —

$$\underset{\text{Milk of Lime}}{Ca(OH)_2} + \underset{\text{Potassium Carbonate}}{K_2CO_3} = \underset{\text{Potassium Hydroxide}}{2\,KOH} + \underset{\text{Calcium Carbonate}}{CaCO_3}$$

It is now manufactured by the electrolysis of a solution of potassium chloride, the process being like the one used for sodium hydroxide.

**Other Potassium Compounds.** — **Potassium Cyanide** (KCN) is a white solid, very poisonous, very soluble in water, and has an odor like bitter almonds. (See Cyanogen, Chapter XVII.) It is used in preparing electroplating solutions and in extracting gold from poor ores. **Potassium Sulphate** ($K_2SO_4$) is manufactured from kainite, and is largely used as a fertilizer and in making potassium carbonate.

**Relation of Potassium to Life.** — Potassium, like nitrogen and phosphorus, is essential to the life of plants and animals. The ash of many common grains, vegetables, and fruits contains potassium as the carbonate. Potassium salts are supposed to assist in the formation of starch, just as phosphorus is indispensable to the transformation of nitrogen compounds. Potassium salts taken from the soil by plants must be returned, if the soil is to be productive. Sometimes crude kainite is used extensively as a fertilizer; but wood ashes, or the sulphate and chloride, are often used to supply potassium salts. (See Relation of Phosphorus to Life, Chapter XXIII.)

**Miscellaneous.** — As already stated, potassium compounds impart a delicate violet tint to a Bunsen flame. Most potassium compounds are soluble in water, and such solutions contain colorless potassium ions ($K^+$). The atomic weight of potassium is 39.10 and the valence is one.

**Lithium**, Li, is a silver-white metal and has the specific gravity of only .534 (at 20° C.), being the lightest of the metallic elements. Its compounds are widely distributed in small quantities in minerals, mineral waters, and plants. Lithia water and citrate of lithium are often prescribed as a remedy for diseases of the kidneys. Lithium compounds color the Bunsen flame a bright red — a delicate test for the element.

**Rubidium**, Rb, and **Cæsium**, Cs, have properties and form compounds analogous to those of potassium.

**The Alkali Metals**, as already stated, form a natural family. The properties of the metals are quite similar, and the chemical activity increases in passing from lithium (at. wt. 7.00) to cæsium (at. wt. 132.81). All decompose water, yielding hydrogen and an hydroxide of the metal. The hydroxides are active bases, and the familiar ones long ago gave the name alkali to the family. Analogous compounds are very much alike; indeed, in many operations, it makes little difference whether sodium or potassium compounds are used, though the former are usually preferred on account of their lower price.

## Ammonium Compounds

**Introduction.** — We found in Chapter XIII that ammonium ($NH_4$) is a metallic radical, *i.e.* a group of elements which acts like an atom of a metal in chemical changes. Its most familiar compound is ammonium hydroxide ($NH_4OH$), which has the properties of a base and resembles sodium and potassium hydroxides. Other compounds of ammonium, especially certain salts, are analogous to the corresponding salts of sodium and potassium. Hence, ammonium compounds, except ammonium hydroxide, are appropriately described in this chapter.

**Ammonium Chloride**, $NH_4Cl$, is prepared by passing ammonia gas into dilute hydrochloric acid, by mixing ammonium hydroxide and hydrochloric acid, or by letting the

two gases mingle. The equation for the essential reaction is —

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric Acid}}{HCl} = \underset{\text{Ammonium Chloride}}{NH_4Cl}$$

It is convenient to regard this compound as the ammonium salt of hydrochloric acid, as if it were formed by replacing the hydrogen of the acid by ammonium, just as sodium forms sodium chloride.

Ammonium chloride is a white, granular, fibrous, or crystalline solid, with a sharp, salty taste. It dissolves easily in water, and in so doing lowers the temperature markedly. When ammonium chloride is heated to a high temperature (about 350° C.), it volatilizes and dissociates into ammonia and hydrogen chloride; these gases reunite to form ammonium chloride as the temperature falls.

Large quantities of ammonium chloride are made at one stage of the manufacture of ammonium hydroxide by passing the gas into hydrochloric acid. The crude product is called "muriate of ammonia" to indicate its relation to muriatic (or hydrochloric) acid. It is largely used in charging Leclanché batteries, as an ingredient of soldering fluids, in galvanizing iron, and in textile industries. The crude salt is purified by heating it gently in a large iron or earthenware pot, with a dome-shaped cover; the ammonium chloride volatilizes easily and then crystallizes in the pure state as a fibrous mass on the inside of the cover, but the impurities remain behind in the vessel. The process of vaporizing a solid substance and then condensing the vapor directly into the solid state is called **sublimation**. It differs from distillation in that the substance does not pass through an intermediate liquid state. The product of sublimation is called a sublimate. Sublimed ammonium chloride is known as *sal ammoniac*.

**Ammonium Sulphate**, $(NH_4)_2SO_4$, is made by passing ammonia gas into sulphuric acid, or by adding ammonium hydroxide to the acid, thus:—

$$\underset{\text{Ammonium Hydroxide}}{2\,NH_4OH} + H_2SO_4 = \underset{\text{Ammonium Sulphate}}{(NH_4)_2SO_4} + 2\,H_2O$$

The commercial salt is a grayish or yellowish solid. It is used as a component of fertilizers, since it is rich in nitrogen, and in making ammonium alum and other ammonium compounds.

**Ammonium Sulphide**, $(NH_4)_2S$, is prepared by passing hydrogen sulphide gas into ammonium hydroxide, thus:—

$$\underset{\text{Hydrogen Sulphide}}{H_2S} + \underset{\text{Ammonium Hydroxide}}{2\,NH_4OH} = \underset{\text{Ammonium Sulphide}}{(NH_4)_2S} + 2\,H_2O$$

The normal sulphide is unstable and forms acid ammonium sulphide (also called ammonium hydrosulphide, $NH_4HS$). Hence, a solution of ammonium sulphide, as usually prepared, contains both the normal and acid sulphide; it smells of hydrogen sulphide and ammonia, and if exposed to the air, it ultimately changes into ammonia, sulphur, and water. A solution of ammonium sulphide is used in qualitative analysis to precipitate as sulphides certain metals of the third group, *e.g.* nickel, cobalt, zinc, and manganese. Ammonium sulphide solutions dissolve sulphur, thereby forming a solution of complex sulphides called **yellow ammonium sulphide**. The latter solution is also used in qualitative analysis. (See Test for Arsenic.)

**Ammonium Nitrate**, $NH_4NO_3$, is made by passing ammonia into nitric acid, or by allowing ammonia gas and the vapor of nitric acid to mingle, thus:—

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Nitric Acid}}{HNO_3} = \underset{\text{Ammonium Nitrate}}{NH_4NO_3}$$

It is a white salt which forms beautiful crystals. It dissolves easily in water with a fall of temperature. When gently heated it decomposes into nitrous oxide ($N_2O$) and water, and its chief use is in the preparation of nitrous oxide (see this compound).

**Ammonium Carbonate** is an impure salt as found in commerce, being a mixture of acid ammonium carbonate ($HNH_4CO_3$) and a related compound. When pure and fresh, it is transparent; but on exposure to air it loses ammonia and turns white. It is used to prepare some kinds of baking powder, to scour wool, as a medicine, and to prepare smelling salts, since it gives off ammonia readily. The solution is used in qualitative analysis to precipitate barium, strontium, and calcium.

**Miscellaneous.** — Most ammonium compounds dissolve in water, and such solutions contain colorless ammonium ions ($NH_4^+$). Attempts to isolate the radical ammonium have thus far failed. The valence of ammonium is one.

Ammonium hydroxide and sodium ammonium phosphate (microcosmic salt) have already been considered.

## Spectrum Analysis

When sodium or one of its compounds is introduced into a Bunsen flame, a vivid yellow color is imparted to the flame; the color yielded by potassium or its compounds is a delicate violet. Many elements, especially the metals, behave similarily. These colors, as already stated, often serve as a simple test for the element (free or combined). But if only a minute amount of the substance is available or an intense color masks a faint one, the test fails or is unreliable; in a few cases, too, the colors are much alike. Nevertheless, it is possible to detect elements in a flame even though the

color is faint or obscured. This is accomplished by the **spectroscope** (Fig. 67). This instrument consists essentially

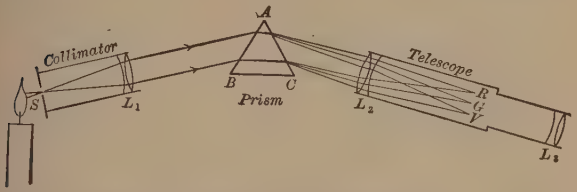



FIG. 67. — Diagram of a spectroscope showing collimator, slit ($S$), telescope, and lenses ($L_1$, $L_2$, $L_3$).

of three parts, (*a*) a tube called the collimator containing a narrow slit at one end through which the light enters, (*b*) a triangular glass prism (placed with its edges parallel to the slit) through which the light passes as it comes from the collimator, and (*c*) a telescope located at such an angle that the light can be viewed as it emerges from the prism.

When ordinary white light, which consists of rays of all colors, enters the slit and falls upon the prism, the rays of light in passing through the prism are bent. That is, the numberless rays making up the white light emerge at an angle to the line along which they entered, the red being bent the least, the violet the most (Fig. 68). Consequently, the emergent light, if caught upon a piece of ground glass or viewed through the telescope, is no longer white, but is a continuous band of colors arranged like the familiar colors of the rainbow. This band of colors consists of a series of colored images of the slit and is called a **spectrum**. The production and examination of a spectrum is termed **spectrum analysis.**

FIG. 68. — Dispersion of light by a prism.

White light contains all the colors of the spectrum. But when colored light, such as that from a sodium or potassium flame, is examined by the spectroscope, instead of the continuous band of colors, we see only those images of the slit which correspond to the rays of light in the sodium or potassium flame. Thus, the sodium flame gives one image of the slit (under usual conditions), which is seen as a brilliant yellow vertical line, besides other and minor ones against a black background; similarly, potassium gives two conspicuous lines, a red and a violet. Each element, if heated to a sufficiently high temperature, has its own series of colored lines, which is called its **line spectrum**. The spectrum of some elements is complex, though many have certain lines which are so conspicuous that the element can be readily detected in a mixture.

In the laboratory the spectroscope is used to detect the presence of certain elements, more especially the metals of the alkali and alkaline earth families. If a small piece of the metal or one of its compounds (preferably the chloride) is put on a platinum wire and held in the Bunsen flame before the slit, the characteristic line spectrum of the element can be readily recognized by looking into the telescope. Several elements can be detected in a mixture, for although certain lines may coincide or overlap, other lines are conspicuous enough to reveal the presence of the components. Minute quantities are detected by the spectroscope, since the light, though too faint to affect the eye, is concentrated by the spectroscope into a bright line (or lines), which stands out against the black background. Consequently rare elements, which can be obtained only in small quantities or with great difficulty, are usually studied spectroscopically. Thus, Bunsen, who (with Kirchhoff) devised the improved spectroscope, discovered and studied the rare metals rubidium and cæsium. Mention has already been made of the

fact that during the last few years the spectroscope has been especially serviceable in studying argon and helium and the related gases.

### Problems and Exercises

1. How much potassium carbonate is necessary to prepare a kilogram of potassium hydroxide? (Assume $K_2CO_3 + Ca(OH)_2 = 2\,KOH + CaCO_3$.)

2. What per cent of Glauber's salt, $Na_2SO_4 . 10\,H_2O$, is sodium sulphate?

3. A gram of gunpowder produced 300 cc. of gas at 0° C. What would be the volume at 2300° C.?

4. How much sodium will 2 kg. of sodium carbonate yield, if heated with carbon? (Assume $Na_2CO_3 + 2\,C = 2\,Na + 3\,CO$.)

5. What is the per cent of sodium in (*a*) NaOH, (*b*) $Na_2SO_4$, (*c*) NaCl, (*d*) $HNaSO_4$?

6. What is the per cent of potassium in (*a*) potassium bromide (KBr), (*b*) potassium nitrate ($KNO_3$), (*c*) potassium iodide (KI)?

7. Suppose 404.186 gm. of sodium chlorate ($NaClO_3$) yield 222.016 gm. of sodium chloride. If 35.46 and 16 are the atomic weights of chlorine and oxygen respectively, what is the atomic weight of sodium?

8. What is the per cent of ammonium ($NH_4$) in (*a*) ammonium chloride ($NH_4Cl$), (*b*) ammonium sulphate, (*c*) ammonium nitrate?

9. What is the formula of a compound containing 26.17 per cent of nitrogen, 7.48 per cent of hydrogen, and 66.35 per cent of chlorine?

10. One hundred grams of potassium chloride give 52.42 gm. of potassium and 47.58 gm. of chlorine. Calculate the atomic weight of potassium (making two assumptions).

11. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): Sodium chlorate, sodium acetate, sodium fluoride, sodium phosphate (ortho), potassium manganate, acid potassium sulphite, lithium carbonate, lithium chloride, lithium phosphate (ortho).

12. Indicate the ions which are in dilute aqueous solutions of the following: Potassium nitrate, ammonium chloride, picromerite, sodium chlorate.

13. Write the ionic equation expressing the interaction of potassium hydroxide and nitric acid.

# CHAPTER XXVI

## Copper — Silver — Gold

**Introduction.** — These metals are related and constitute a family in Group I of the periodic classification, but they do not have such marked family characteristics as the alkali metals. The metals, as well as their alloys and compounds, have many domestic and commercial uses.

### Copper

**Copper** has been known for ages. Domestic utensils and weapons of war containing copper were used before similar objects of iron. The Romans obtained copper from the island of Cyprus. They called it *cuprium aes* (*i.e.* Cyprian brass), which finally became simply *cuprum*. From *cuprum* we obtain the symbol Cu and the terms *cuprous* and *cupric*.

**Occurrence of Copper.** — Copper, both free and combined, is an abundant element. Single masses of native or metallic copper weighing many tons are found in the Michigan mines on the shores of Lake Superior. Besides the native copper, the most valuable ores are copper sulphide (chalcocite or copper glance, $Cu_2S$), copper oxide (cuprite or ruby ore, $Cu_2O$), the copper-iron sulphides (copper pyrites or chalcopyrite, $CuFeS_2$, and bornite, $Cu_3FeS_3$), and the basic carbonates (malachite, $CuCO_3 . Cu(OH)_2$, and azurite, $2\,CuCO_3 . Cu(OH)_2$).

Native copper comes chiefly from Michigan, the copper-iron sulphide ores from Montana, and the oxide and carbonates from Arizona.

**Metallurgy of Copper.** — Copper is extracted from its ores by processes which vary with the composition of the ore. (1) Native copper ore is first crushed, then washed to remove rocky impurities, and the concentrated product finally melted. (2) The carbonates and oxide are reduced by roasting them with coke in a blast furnace. The general chemical change is reduction and may be represented thus: —

$$\underset{\text{Copper Oxide}}{Cu_2O} + \underset{\text{Carbon}}{C} = \underset{\text{Copper}}{2\,Cu} + \underset{\text{Carbon Monoxide}}{CO}$$

(3) The smelting of copper-iron sulphides is a complicated process. The ore is crushed and washed, and then roasted in a furnace. This operation removes the adhering rock and changes much of the sulphide into an oxide. The roasted mass is next heated with coal and sand in a shaft or a reverberatory furnace, whereby the iron is largely changed into a fusible silicate which runs off as a slag. The remaining "matte," as it is called, contains from 50 to 65 per cent of copper besides iron, sulphur, and arsenic, and is further treated in one of two ways. (*a*) It is roasted and melted until all the iron and arsenic are removed and mainly copper sulphide remains. This is finally roasted to convert it partly into an oxide, and the mixture of sulphide and oxide is again melted; the sulphur passes off as sulphur dioxide, and the copper is left behind. The equation for this final change is —

$$\underset{\text{Copper Oxide}}{2\,CuO} + \underset{\text{Copper Sulphide}}{Cu_2S} = \underset{\text{Copper}}{4\,Cu} + \underset{\text{Sulphur Dioxide}}{SO_2}$$

(*b*) Sometimes after the ore has been roasted the removal of the iron, sulphur, and arsenic is hastened by pouring the impure copper into a vessel shaped like a Bessemer converter and lined with silica (only smaller), and then forcing

hot air through the molten mass. The refined copper is cast into thick plates called anodes and purified by electrolysis.

**Purification of Copper.** — The anodes are connected with the positive electrode of a powerful battery or dynamo and suspended in a solution of copper sulphate and sulphuric acid. Sheets of pure copper are made the cathodes and dip into the solution as shown in Figure 69. When the current passes, pure copper leaves the anodes and becomes deposited upon the cathodes; the impurities either remain in solution or fall to the bottom of the tank as a slime, from which gold and silver are extracted in appreciable quantities. The operation can be interpreted by principles already discussed. The copper ions ($Cu^{++}$) migrate to the cathode, where they lose their electric charges and are deposited as metallic copper (Cu). The $SO_4$-ions ($SO_4^{--}$) migrate to the anode, where they likewise lose their charges, become ordinary chemical $SO_4$-groups, and unite with copper from the anode to form $CuSO_4$, which, however, immediately ionizes into $Cu^{++}$ and $SO_4^{--}$. The gold and silver do not ionize and the zinc (if present) remains in the solvent as ionic zinc ($Zn^{++}$). Thus the solution is constantly supplied with ions of copper and $SO_4$, and pure copper is removed from the anodes and deposited in equivalent amounts upon the cathodes. New anodes and cathodes are supplied as needed. Electrolytic copper, as it is often called, is exceedingly pure.

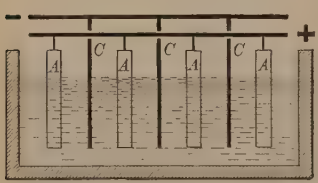



FIG. 69. — Apparatus for the preparation of pure copper by electrolysis. *A*, *A*, *A* are anodes, and *C*, *C*, *C* are cathodes.

**Properties of Copper.** — Copper is a bright metal, distinguishable from all others by its peculiar reddish color. It is flexible, hard, and tough; its malleability and ductility allow it to be drawn out into wire and rolled into very thin sheets. Its specific gravity varies slightly with the method of treatment, but is about 8.9. The melting point is about 1060° C. Copper is an excellent conductor of both heat and electricity. In dry air, it turns dull; and in moist air it gradually becomes coated with a greenish basic copper carbonate. Heated in the air, it is changed into the black copper oxide, and at a high temperature it colors a flame emerald green. Copper does not liberate hydrogen readily from dilute acids. With nitric acid it forms copper nitrate and oxides of nitrogen (see Oxides of Nitrogen); with hot concentrated sulphuric acid it yields copper sulphate and sulphur dioxide (see Sulphur Dioxide). Hydrochloric acid has little effect upon it. Copper replaces certain metals if suspended in solutions of their compounds, *e.g.* a clean copper wire soon becomes coated with mercury, if placed in a solution of any mercury compound; on the other hand, certain metals, such as iron, zinc, and magnesium, remove copper from its solution, *e.g.* a nail or knife blade soon becomes coated with copper if dipped into a solution of any copper compound. Scrap iron is sometimes used to precipitate copper on a large scale. (See Displacement of Metals below.)

**Uses of Copper.** — Next to iron, copper is the most useful metal. Enormous quantities of wire are used in operating the telegraph, cable, telephone, electric railway, and electric light. Sheet copper is made into household utensils, boilers, and stills. Copper bolts, nails, rivets and sheathing are used on ships, because copper is only slowly corroded by moist air and salt water. All nations use copper as the

chief ingredient of small coins. Electrical apparatus utilizes much copper. Maps, etchings, and some kinds of engravings are printed from copper plates; calico is printed from a copper cylinder upon which the design is engraved. Books are printed and illustrated from electrotypes, made by depositing a film of copper upon an impression of the type or design in wax. In a similar way many objects are copper plated. (See Electrotyping and Electroplating, Chapter XI.)

**Alloys of Copper** are important. **Brass** is a bright yellow alloy containing 63 to 72 per cent of copper, the remainder being zinc. It is made by melting these metals together. It can be drawn into wire, hammered into any shape, and turned in a lathe. It is harder than copper, and melts at a lower temperature. On account of its durability, elasticity, and other properties, it has many uses for which copper and zinc are not suited. Pinchbeck, Muntz metal, Bath metal, Dutch metal (leaf or "gold"), are varieties of brass. Muntz metal is often used in place of sheet copper as sheathing for the bottoms of ships, because it becomes corroded very slowly. Typical **bronze** contains different proportions of copper, zinc, and tin; some antique bronzes contain lead or iron. The per cent of copper is 70 to 95, of zinc 1 to 25, of tin 1 to 18. The proportions in the British bronze coinage are copper 95, zinc 1, tin 4. On account of its fusibility, beautiful color, and extreme durability, bronze is used for statues, memorial tablets, coins, and medals. The ancients made it into weapons of war and household utensils. Cannon were formerly made of bronze, but for this purpose steel is now used. Phosphor bronze contains a small per cent of phosphorus and tin, and manganese bronze about 30 per cent of manganese; they are tougher than ordinary bronze, and are used to make steamship propellers and parts of

machines. Silicon bronze is copper with traces of iron and silicon; its tenacity makes it especially serviceable for telegraph, trolley, and telephone wires. Aluminium bronze contains 90 to 95 per cent copper, the rest being aluminium. It is a hard, yellow-brown, elastic alloy, and is used in constructing hulls of yachts; its lightness, strength, and resistance to chemicals adapt it to many other uses.

**Gun metal** is about 90 per cent copper and 10 per cent zinc; it was formerly used in making cannon, and is now used to some extent in making firearms. **Bell metal** contains about 75 per cent copper and 25 per cent zinc. **Speculum metal** contains about 70 per cent copper, 30 per cent tin, and traces of zinc, nickel, and iron; it takes a brilliant polish and is used in optical instruments. The numerous varieties of **German silver** contain different proportions of copper, nickel, and zinc. The per cent of copper is 50 to 60, of nickel 20 to 25, and of zinc about 20. In color and luster it resembles silver, for which it is often substituted. Its power to conduct electricity is only slightly affected by changes of temperature, hence it is often used in resistance coils. Chinese Pakfong (or paktong) is a variety of German silver. The **nickel coins** of Germany and the United States contain 75 per cent copper and 25 per cent nickel. Copper is also a constituent of many other coins. Britannia metal and white metal, in which copper is the minor constituent, are described under Alloys of Tin.

**Compounds of Copper.** — Copper forms two series of compounds, the cuprous and the cupric. Thus, there are cuprous oxide ($Cu_2O$) and cupric oxide ($CuO$), cuprous chloride ($CuCl$) and cupric chloride ($CuCl_2$). The cuprous compounds contain a larger proportion of copper than the corresponding cupric compounds. The valence of copper is one in the cuprous series and two in the cupric. Not every member of each series, however, is important or even well known. Solutions of cupric compounds contain cupric ions ($Cu^{++}$) and those of cuprous compounds contain cuprous ions ($Cu^{+}$). Copper compounds are poisonous. Cooking utensils made of copper should be used with care; vege-

tables, acid fruits, and fruit preserves, if boiled in such vessels, should be removed as soon as cooked. The vessels themselves should be kept bright to prevent the formation of soluble copper salts which might contaminate the contents.

**Cuprous Oxide**, $Cu_2O$, occurs native as cuprite or ruby ore. It can be obtained as reddish powder by heating a mixture of solutions of copper sulphate, Rochelle salt (potassium sodium tartrate), sodium hydroxide, and glucose. This oxide colors glass ruby red. It is a beautiful mineral and a valuable ore.

**Cupric Oxide**, CuO, is a black solid formed by heating copper in a current of oxygen or by heating copper nitrate or other cupric salts intensely. It is reduced to metallic copper when heated in a current of hydrogen or with substances containing hydrogen or carbon, thus: —

$$\underset{\text{Copper Oxide}}{CuO} + \underset{\text{Hydrogen}}{H_2} = \underset{\text{Copper}}{Cu} + \underset{\text{Water}}{H_2O}$$

This property has led to its use in determining the amount of hydrogen or carbon in compounds. (See also Gravimetric Composition of Water.)

**Copper Sulphate** or **Cupric Sulphate**, $CuSO_4$, is the most useful compound of copper. It is a blue, crystalline solid, and is often called blue vitriol or bluestone. The crystallized salt ($CuSO_4 . 5\,H_2O$) loses water slowly in the air; heated to 240° C., all the water escapes, leaving a whitish powder. This anhydrous copper sulphate, as it is often called, absorbs water from alcohol and similar liquids; and when added to water, it again becomes blue. An aqueous solution of copper sulphate has an acid reaction. As already stated, this is due to hydrolysis. The cupric ions ($Cu^{++}$) combine with

hydroxyl ions (from the slightly dissociated water) to form the slightly dissociated cupric hydroxide ($Cu(OH)_2$). This removal of OH-ions, although slight, leaves in the solution enough hydrogen ions ($H^+$) to turn blue litmus to red. (See Hydrolysis, Chapter X.)

Copper sulphate is used in electric batteries, in making other copper salts, in calico printing, dyeing, copper plating, in preserving timber; recently very dilute solutions have been used to destroy certain forms of objectionable organic matter in drinking water. It is a germicide and is one ingredient of certain mixtures (such as Bordeaux mixture) which are sprayed upon trees to destroy fungi and kill insects.

Copper sulphate is prepared on a large scale by treating copper with dilute sulphuric acid, the equation for the chemical change being —

$$\underset{\text{Copper}}{2\,Cu} + \underset{\text{Sulphuric Acid}}{2\,H_2SO_4} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Copper Sulphate}}{2\,CuSO_4} + \underset{\text{Water}}{2\,H_2O}$$

Until recently much of the copper sulphate of commerce was obtained as a by-product in refining gold and silver with sulphuric acid (see below).

**Copper Nitrate**, $Cu(NO_3)_2$, is a blue, crystalline solid, formed by the interaction of dilute nitric acid and copper or copper oxide. It is a cupric salt. It is deliquescent, very soluble in water, and is readily decomposed by heat into cupric oxide and oxides of nitrogen.

**Cuprous Sulphide**, $Cu_2S$, is the bluish black mineral chalcocite. **Cupric sulphide**, CuS, is the black precipitate formed by the interaction of hydrogen sulphide and a cupric salt.

**Copper Carbonates.** — Malachite ($CuCO_3 . Cu(OH)_2$) and azurite ($2\,CuCO_3 . Cu(OH)_2$) are basic carbonates. Both occur as minerals,

malachite being bright green and azurite a magnificent blue. They are valuable ores of copper. Malachite is easily polished and is used as an ornamental stone for pillars, mosaics, and table tops.

**Copper Acetates.**—Verdigris is copper acetate ($Cu_3(OH)_2 . (C_2H_3O_2)_4$), which is used to some extent in making green paint and Paris green. The latter is copper aceto-arsenite and is used to exterminate potato bugs and other insects. Verdigris is a basic salt.

**Copper-Ammonia Compounds.** — When a little ammonium hydroxide is added to the solution of a copper salt, a whitish, gelatinous precipitate is formed which upon the addition of an excess of ammonium hydroxide becomes a deep blue solution. If cupric sulphate is used, complex compounds can be obtained from this solution, *e.g.* $Cu(NH_3)_4SO_4$. The blue color of the solution is believed to be due to the complex ion $Cu(NH_3)_4^{++}$.

**Tests for Copper.** — (1) The reddish color, peculiar "coppery" taste, and green color imparted to a Bunsen flame serve to identify metallic copper. (2) An excess of ammonium hydroxide added to the solution of a copper compound produces a deep blue solution. (3) A few drops of acetic acid and of potassium ferrocyanide solution added to a dilute solution of a copper compound produce a brown gelatinous precipitate of cupric ferrocyanide ($Cu_2Fe(CN)_6$).

**Displacement of Metals.** — The deposition of metallic copper when certain metals are put into solutions of copper salts and the displacement of mercury from solutions of its salts by metallic copper itself are examples of a kind of chemical change in which most metals can participate. Thus, lead displaces silver and copper, while zinc displaces lead and tin. But lead does not displace aluminium, nor does copper displace cadmium. The displacing relations of metals, so to speak, have been carefully studied and the familiar metals can be arranged in a series called the —

ELECTROCHEMICAL SERIES OF THE METALS

| | | |
|---|---|---|
| Magnesium | Cobalt | Copper |
| Aluminium | Nickel | Mercury |
| Zinc | Tin | Silver |
| Cadmium | Lead | Platinum |
| Iron | Hydrogen | Gold |

In this series each free metal displaces the succeeding metals from their solutions, and is in turn displaced from solution by those metals which precede. For example, zinc (except when very pure), being near the beginning, displaces most of the metals in the series, while copper, being near the end, displaces only a few.

When zinc displaces copper from a copper sulphate solution, the zinc passes into solution and can be recovered as zinc sulphate. Since zinc sulphate dissociates in solution into zinc ions ($Zn^{++}$) and $SO_4$-ions ($SO_4^{--}$), we may describe the change in the zinc as a transformation from neutral atomic zinc (Zn) into ionic zinc ($Zn^{++}$). Furthermore, 63.57 gm. of metallic copper are deposited when 65.37 gm. of metallic zinc have passed into solution. These quantities are identical with the atomic weights of these elements. So that zinc displaces copper atom for atom. Hence we may write the chemical change thus: —

$$Zn + Cu^{++} + SO_4^{--} = Cu + Zn^{++} + SO_4^{--}$$

or briefly

$$Zn + Cu^{++} = Cu + Zn^{++}$$

All metals are like zinc in having a tendency to pass from the atomic state into the ionic or dissolved state. Moreover, this solution tension, as it is sometimes called, is capable of measurement. It has been found that the magnitude of solution tension decreases as we pass from

magnesium, which is the most electro-positive, to gold, which is the least electro-positive in the list.

Hydrogen is not a metal in the common acceptance of this term, but hydrogen ions ($H^+$) are positive, so hydrogen is usually included in the electrochemical series of the metals. Its position is interesting. All the metals that precede hydrogen displace it from most acids, while those that follow do so rarely, if at all. That is, hydrogen is displaced from its solutions only by metals which have a greater solution pressure, behaving in this respect like other members of the series.

## Silver

**Silver** is one of the oldest metals. For ages it has been used in the form of ornaments, costly vessels, and coins. It is a noble metal, *i.e.* one which does not oxidize readily in the air. The Latin name of silver is *argentum*, from which the symbol Ag is derived. The alchemists called it *luna* on account of its silvery or "moonlike" appearance, and its alchemistic symbol was a crescent.

**Occurrence of Silver.** — Native silver is found in Arizona, Mexico, Norway; also in South America and Australia. The chief ores are the sulphides. The simple sulphide (silver glance or argentite, $Ag_2S$) is the richest ore, and is found alone in many localities in the United States; it also occurs mingled with sulphides of lead, copper, antimony, or arsenic. These complex sulphides are found in Mexico, Peru, Bolivia, Chili, and in Idaho. Small quantities of native silver chloride (horn silver, AgCl) are also found; it resembles wax or horn in softness and color. Alloys of silver with gold, mercury, and copper are found; average California gold contains about 12 per cent silver. Many ores contain silver, especially those of lead; and this argen-

tiferous (or silver-bearing) lead is one of the chief sources of silver.

**Metallurgy of Silver.** — Silver is extracted from its ores by two principal processes. (1) In the amalgamation process the powdered ore is first changed into silver chloride by roasting (or simply mixing) it with sodium chloride. The mass is then reduced to silver by agitation with water and iron (or an iron compound); the simplest equation for this reaction is: —

$$\underset{\text{Silver Chloride}}{2\,AgCl} + \underset{\text{Iron}}{Fe} = \underset{\text{Silver}}{2\,Ag} + \underset{\text{Iron Chloride}}{FeCl_2}$$

The silver is removed by adding mercury, which forms an amalgam with the silver, but not with the other substances. When the amalgam is heated, the mercury distills off, and the silver — with some gold — remains behind. (2) Silver is extracted from lead ores by the Parkes process. After the sulphur, arsenic, and other impurities have been removed from the lead ores, the final product is a mixture of lead, silver, and gold. This is melted and thoroughly mixed with zinc. As the mixture cools, an alloy of silver, gold, zinc, and a little lead rises to the top, solidifies, and is removed. The remaining lead mixture is treated again with zinc. The alloy of silver, gold, zinc, and lead is heated to volatilize the zinc and to oxidize (or to melt away) the lead. The silver and gold are separated by electrolysis or by heating the mixture with sulphuric acid; the gold is not acted upon in the latter process, but the silver forms silver sulphate, which is reduced by copper to metallic silver.

Lead ores containing considerable silver are sometimes subjected to **cupellation** to extract the silver. The ore or alloy is heated in a furnace having a shallow hearth made of porous, infusible bone ash. The lead is thereby changed into an oxide (PbO, litharge), which melts, and is partly

driven off by the air blast into pots and partly absorbed by the porous cupel. The silver is prevented from oxidizing by the melted litharge, but toward the end of the operation the thin film of litharge bursts, and the metallic silver appears as a bright disk, if the operation is conducted in a furnace, and as a globule or button, if the extraction is performed in a small assay cupel. The process is then stopped and the silver removed.

**Properties of Silver.** — Silver is a lustrous, white metal, which takes a brilliant polish. It is harder than gold, but softer than copper. Like copper, it is tenacious, ductile, and malleable, and can be easily made into various shapes. Its specific gravity is about 10.5. It melts at about 962° C., and fuses readily on charcoal in the blowpipe flame; it vaporizes in the oxyhydrogen flame and in the electric furnace. Molten silver absorbs about twenty times its volume of oxygen, which is expelled violently when the silver solidifies. Silver is an excellent conductor of heat and electricity, but it is too expensive for such uses. It does not tarnish in air, unless sulphur compounds are present (especially hydrogen sulphide), and then the familiar brown or black film of silver sulphide is produced. This blackening is especially noticed on silver spoons which have been put into eggs or mustard, and on silver coins which have been carried in the pocket, the sulphur in the latter case coming from the sulphur compounds in the perspiration; the tarnishing of household silver is due to sulphur compounds in illuminating gas or the gas from burning coal. So-called "oxidized" silver is not oxidized, but coated with silver sulphide. Silver is only very slightly acted upon by hydrochloric acid, and not at all by melted potassium hydroxide, sodium hydroxide, or potassium nitrate; this indifference has led to the use of silver crucibles in analytical processes involving such

caustic substances. Nitric acid and hot concentrated sulphuric acid change it into the nitrate and sulphate respectively.

**Alloys of Silver.** — Pure silver is too soft for constant use, so is usually hardened by adding a small amount of copper. These alloys are used in making coins and jewelry. The silver coins of the United States and France contain 900 parts of silver to 100 of copper, and are called 900 fine. British silver coins are 925 fine; this quality is called "sterling silver," and from it much ornamental and useful silverware is made.

**Silver Plating.** — Metals cheaper than silver can be coated or plated with pure silver precisely as in the case of copper. Plated silverware has the appearance of solid or pure silver. The object to be plated is carefully cleaned, and made the cathode in an electrolytic cell containing a solution of potassium silver cyanide ($KAg(CN)_2$). The anode is a plate of pure silver (Fig. 70). The coherent deposit of silver is dull, but can be brightened by rubbing with or without chalk.

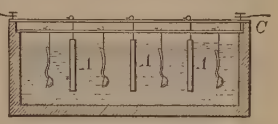


FIG. 70. — Apparatus for silver plating. *A*, *A*, *A* are silver anodes, and the spoons are cathodes.

**Compounds of Silver.** — The most important compound is **silver nitrate** ($AgNO_3$). It is a white, crystalline solid, readily soluble in water. It is made by treating silver with nitric acid. The equation for the chemical change is: —

| $3\,Ag$ | + | $4\,HNO_3$ | = | $3\,AgNO_3$ | + | $NO$ | + | $2\,H_2O$ |
|---|---|---|---|---|---|---|---|---|
| Silver | | Nitric Acid | | Silver Nitrate | | Nitric Oxide | | Water |

Exposed to the light, it turns dark if in contact with organic matter. It discolors the skin; if applied long enough, it disintegrates the flesh, and is often used by physicians for this purpose. Its caustic action and the silvery color of the metal from which it is made long ago led to the name, lunar caustic. Besides its extensive use in photography and silver plating, silver nitrate is the essential constituent of some indelible inks. **Silver chloride** (AgCl) is made by adding hydrochloric acid or any soluble chloride to a solution of a silver compound. Thus formed, it is a white, curdy solid, which turns violet in the light, and finally black. This action of light is more intense if organic matter is present. Silver chloride is only slightly soluble in water, but it dissolves in ammonium hydroxide, in sodium thiosulphate solution, and in potassium (or sodium) cyanide solution; in each case a complex compound is produced. The formation and properties of silver chloride constitute the **test for silver.** **Silver bromide** (AgBr) and **silver iodide** (AgI) are similar to silver chloride in their properties. Silver bromide is slightly yellow and silver iodide has a distinct yellow tinge; compared with the chloride, both are less soluble in ammonium hydroxide; the bromide dissolves readily and the iodide only slightly in sodium thiosulphate solution. Silver bromide and iodide find extensive application in photography.

Silver compounds, if soluble in water, yield silver ions ($Ag^+$). Complex ions are formed with other solvents, *e.g.* $Ag(NH_3)_2^+$ with an excess of ammonium hydroxide and $Ag(CN)_2^-$ with an excess of potassium cyanide solution.

The atomic weight of silver is 107.88 and the valence is one.

**Photography** is based on the fact that silver salts, especially the bromide, change chemically when mixed with organic matter and exposed to the light. The photograph

is taken on a glass plate, coated on one side with a thin layer of gelatine, containing the silver salt. Sometimes a sheet of sensitized gelatine, called a film, is used. The plate or film is placed in the camera and **exposed.** The light, which is reflected from the object being photographed, changes the silver salt in proportion to its brilliancy. The plate, however, shows no change until it has been **developed.** This process consists in treating the plate with a reducing agent, *e.g.* ferrous sulphate, pyrogallic acid, or special mixtures. As the developer acts upon the silver salt, the image appears. This is really a deposit of finely divided silver. Where the intense light fell upon the plate, the deposit is heavier than where little or no light fell. Hence, dark parts of the object appear light on the plate, and light parts dark; and since the image is the reverse of the object, the plate is called a negative. When the plate has been properly developed, it still contains some silver salt not altered by the light; and if it were left on the plate, the image would be clouded and finally obliterated by the light. The image is, therefore, **fixed** by washing off the unchanged silver salt with a solution of sodium thiosulphate (or "hyposulphite"). A print is made by laying sensitized paper upon the negative and exposing them to the sunlight, so that the light will pass through the negative to the paper. The negative obstructs the light in proportion to the thickness of the silver deposit, so the photograph has the same shading as the object. Most prints, like the plates, must be fixed. Sometimes the color is improved by toning, *i.e.* by placing the print in a solution of gold or of platinum.

**Gold**, like silver, is one of the oldest metals. For ages it has been the most highly prized of the metals and exten-

sively used for personal adornment and for the fundamental standard of value. Chemically it is a noble metal.

The Latin name of gold, *aurum*, gives the symbol Au. For several centuries the mediæval chemists or alchemists tried to produce gold by the transmutation of base or cheaper metals. They were unsuccessful in their search for the philosopher's stone, which they believed had power to effect this transformation.

**Occurrence of Gold.** — Gold is widely distributed in the native state, but not abundantly in many places. Unlike copper and silver, its compounds are few and rare; the only important ones are the tellurides (compounds of tellurium, *e.g.* $AuAgTe_2$) found in Colorado. Gold is never found pure, being alloyed with silver and occasionally with copper or iron. It is disseminated in fine, almost invisible, particles among ores of other metals, especially the sulphides of copper and iron, though not so abundantly as silver. Much gold is found in veins of quartz, and in the sand and gravel formed from gold-bearing rocks. Gold occurs usually as dust, scales, or grains, but occasionally shapeless masses called "nuggets" are found, varying in weight from a few grams to many kilograms. The largest nugget ever known weighed about 84 kg. (184 lb.).

The chief gold-producing countries are the United States, Australia, South Africa, and Russia. The annual production in the United States is about four million troy ounces, which comes largely from Colorado, California, other Western states, and Alaska.

**Gold Mining and Metallurgy.** — Gold was first obtained by miners by washing the gold-bearing sand and gravel of a stream in large pans or cradles. This primitive method was soon replaced by placer mining and hydraulic mining. Streams of water, directed against the earth containing the

gold, wash away the lighter materials, but leave the heavy gold behind as fine particles called gold dust. From this mixture gold and silver are extracted by mixing with mercury, or by passing the moistened mass over copper plates coated with mercury. The amalgam is then heated, as in the metallurgy of silver, to remove the mercury; the residue of gold and silver is separated as described below. In vein mining the gold-bearing rock — usually quartz — is crushed and then washed, and the gold removed by mercury, as in placer mining. Low grade ores and those containing certain metals cannot be profitably treated with mercury. In the chlorination process the crushed ore is roasted and then revolved in barrels containing bleaching powder and sulphuric acid; this operation forms a soluble gold chloride ($AuCl_3$), from which the gold is precipitated as a fine powder by ferrous sulphate (or other reducing agents). Sometimes liquid chlorine is used in the chlorination process. In the cyanide process the crushed ore, or the slime from a previous extraction, is mixed with a weak solution of potassium (or sodium) cyanide in large vats exposed to the air; this operation changes the gold into a soluble cyanide, thus: —

$$\underset{\text{Gold}}{4\,Au} + \underset{\substack{\text{Potassium}\\\text{Cyanide}}}{8\,KCN} + \underset{\text{Oxygen}}{O_2} + \underset{\text{Water}}{2\,H_2O} = \underset{\substack{\text{Potassium}\\\text{Gold Cyanide}}}{4\,KAu(CN)_2} + \underset{\substack{\text{Potassium}\\\text{Hydroxide}}}{4\,KOH}$$

The gold is separated from this solution by electrolysis or by treatment with zinc.

**Purification of Gold.** — Gold obtained by the foregoing methods is impure, silver being the chief impurity. These metals were formerly parted by a chemical process, but they are now separated by electrolysis. By the old parting process known as quartation an alloy of gold and silver, in which gold is about one fourth of the whole, is treated with

nitric acid; this operation changes the silver into the nitrate, from which the pure gold can be readily removed. The metals can also be parted by the cheaper method described under silver, viz. by boiling with concentrated sulphuric acid. By this treatment the gold, which is about one sixth of the alloy, is left as a brownish, porous mass. It is washed and dried, and then fused into a coherent mass with charcoal and sodium carbonate. These chemical processes have been largely displaced by electrolytic methods of separation. In one of the latter the anode is an alloy of gold and silver (low in gold), the cathode is silver, and the electrolytic solution is a dilute silver nitrate solution containing a small proportion of nitric acid. When the current passes, part of the silver of the anode goes into solution as the nitrate, while part is deposited at the cathode; the gold remains at the anode as a fine powder and is caught in a cloth bag which incloses the whole anode. In another electrolytic process, which is successfully operated in the United States mints, the anode is an alloy rich in gold, the cathode is pure gold, and the electrolytic solution is a solution of gold chloride ($AuCl_3$) and hydrochloric acid; very pure gold is deposited on the cathode, while the silver forms silver chloride around the anode.

The purity of gold is expressed in **carats**. Pure gold is 24 carats fine; an alloy containing 22 parts of gold and 2 parts copper is 22 carat gold, while one containing equal parts gold and other metals is 12 carat gold.

**Properties of Gold.** — Gold is a lustrous, yellow metal. It is about as soft as lead, and is the most ductile and malleable of all metals. The leaf into which it is readily beaten is very thin. The melting point is 1063° C. Gold is one of the heaviest metals, its specific gravity being about 19. Air, oxygen, hydrogen sulphide, water vapor, and the common

acids do not attack it; but it is changed into a gold chloride ($AuCl_3$) by chlorine water and compounds and mixtures which liberate chlorine, especially a mixture of concentrated nitric and hydrochloric acids. This mixture, long known as *aqua regia*, has already been discussed. (See *Aqua Regia*.)

**Uses of Gold.** — Pure gold is too soft for most practical uses, and is therefore usually hardened by adding copper or silver. The gold-copper alloy has a reddish color and is often called "red gold"; the gold-silver alloy is paler than pure gold and is sometimes called "white gold." Gold coins contain gold and copper. The United States standard gold coins contain 9 parts gold and 1 part copper, while in England the legal standard is 11 of gold to 1 of copper. Gold leaf of various grades is used to ornament books, signs, and other objects. Jewelers use gold for many purposes; such gold varies from 12 to 22 carats in purity. On account of its malleability, feeble chemical action, and beauty, gold is used by dentists for filling teeth.

**Compounds of Gold** are readily decomposed by metals, reducing agents (*e.g.* ferrous sulphate or hydrogen sulphide), fine solids like charcoal, and by electrolysis. When gold is dissolved in *aqua regia* and the excess of acid removed by evaporation, the resulting auric chloride ($AuCl_3$) gives with stannous chloride solution a beautiful purple precipitate; the latter is called "purple of Cassius," and is finely divided gold. Its formation is a **test for gold**. The process of gold plating is the same as silver plating, only the solution is one of potassium auricyanide ($KAu(CN)_4$) and the anode is gold. Much cheap jewelry is gold plated.

The atomic weight of gold is 197.2.

**The Copper Family** belongs to Group I in the periodic classification, but it is not a typical family. Not only are

these elements quite different from the other family in this group (*i.e.* the alkali metals), but the different members are not closely related to each other. Indeed copper more closely resembles mercury and iron than it does silver, while gold has properties which strongly suggest aluminium and iron. The valence of copper, as already stated, is one in cuprous compounds and two in cupric. The valence of silver is usually one. Gold has the valence of one in aurous compounds and three in auric compounds.

### Problems and Exercises

1. How much cupric oxide is formed by heating 1467 gm. of copper in air? (Assume $Cu + O = CuO$.)

2. Calculate the per cent of copper in (*a*) malachite ($CuCO_3 . Cu(OH)_2$), (*b*) azurite ($2\,CuCO_3 . Cu(OH)_2$), (*c*) copper sulphate ($CuSO_4$).

3. If 480 gm. of silver interact with nitric acid, how much silver nitrate is formed?

4. Calculate the per cent of silver in (*a*) silver chloride ($AgCl$), (*b*) silver sulphide ($Ag_2S$), (*c*) silver nitrate ($AgNO_3$).

5. If 10 gm. of silver are changed into silver nitrate, how many cubic centimeters of hydrochloric acid solution (sp. gr. = 1.2 and containing 33 per cent $HCl$) will be needed to precipitate all the silver as silver chloride?

6. An alloy containing 90 per cent of silver and 10 per cent of copper is dissolved in nitric acid. The original weight was 260 gm. How many grams of zinc are needed to displace the silver and copper?

7. Suppose 4.393 gm. of copper precipitate 14.91 gm. of silver from a silver nitrate solution. If the atomic weight of silver is 107.88, what is the atomic weight of copper?

8. Suppose 20.6885 gm. of copper oxide ($CuO$) yield 16.5167 gm. of copper by reduction with hydrogen; what is the atomic weight of copper?

9. Write the formulas of the following compounds by applying the principle of valence (see Chapter XIV): Cuprous iodide, cupric acetate, silver cyanide, silver sulphate, silver oxide, aurous bromide, auric chloride, aurous hydroxide, cupric hydroxide, cuprous sulphide, cuprous nitrate.

10. Write the ionic equation for the hydrolysis of copper sulphate.

## CHAPTER XXVII

### Calcium, Strontium, and Barium — Radium

These elements form a natural family in Group II of the periodic classification, and are known as the alkaline earth metals. The compounds of calcium are numerous and useful.

### Calcium

**Occurrence.** — Calcium is never found free. Combined calcium makes up about 3.5 per cent of the earth's crust. The most abundant compound is calcium carbonate ($CaCO_3$). This has many familiar forms, *e.g.*, limestone, chalk, marble, coral, and shells. Many rocks are complex silicates of calcium and other metals. The extensive deposits of calcium phosphate and calcium borate have already been mentioned. Calcium sulphate ($CaSO_4$) occurs abundantly in the form of gypsum, alabaster, and selenite. Calcium compounds are essential to the life of plants and animals, being found in the leaves of plants, and in the bones, teeth, and shells of animals. The ocean, many rivers, lakes, and springs contain calcium salts, especially the acid carbonate ($H_2Ca(CO_3)_2$) and the sulphate.

**Preparation.** — Impure calcium was prepared by Davy in 1808, and a pure sample was obtained in 1898 by Moissan by the reduction of calcium iodide by sodium. The metal is now prepared by the electrolysis of fused calcium chloride. The anode is a graphite crucible and the cathode is a rod of iron or copper which can be elevated by a screw. As soon as the current passes through the fused calcium chloride

metallic calcium collects on the end of the cathode and is removed as an irregular rod by slowly raising the cathode; the end of the calcium rod dips into the electrolyte and thus serves as the lower end of the original cathode.

**Properties.** — Calcium is a white, lustrous metal. It is harder than lead but softer than zinc. It tarnishes slowly in the air. When heated, it unites with oxygen, hydrogen, and nitrogen, forming respectively the oxide, hydride ($CaH_2$), and nitride ($Ca_3N_2$). The interaction with water, which is rapid though not violent, produces hydrogen and calcium hydroxide. The interaction with dilute acids, however, is vigorous.

**Calcium Carbonate**, $CaCO_3$. — The most abundant form of this compound is **limestone**. Vast deposits are found in many places and exhibit a variety of textures and colors. In the United States much limestone is found in Iowa, Illinois, and Wisconsin. All kinds are compact and usually soft, though some are hard enough for use as building stone; some are coarse, and often consist of grains, crystals, or small shells. Pure limestone is a white or gray compact solid, but impurities, especially organic matter and iron compounds, produce blue, yellow, reddish, and black varieties. Hard, crystalline limestone which takes a good polish is called **marble**. This form, which has a wide range of color, is used as a building and an ornamental stone. **Calcite** is crystallized calcium carbonate. It is almost as abundant as quartz, though softer; its varied color and crystal form combine to make it an attractive mineral (Fig. 71). A very transparent variety of calcite called Iceland spar has the remarkable property of double refraction, *i.e.* making small objects appear double.

Calcium carbonate is not soluble in water, unless carbon dioxide is present. (See also Carbon Dioxide and Acid Cal-

cium Carbonate.) As water containing carbon dioxide works its way underground in limestone regions, the limestone is dissolved and caves are often formed or enlarged. When the water enters a cave and drips from the top, the water evaporates, or the gas escapes, or both, and the calcium carbonate is redeposited, often forming stalactites and stalagmites. The stalactites hang from the roof like icicles, while

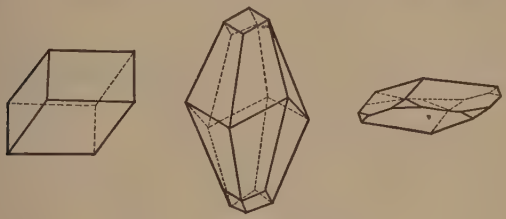


Fig. 71. — Calcite crystals.

the stalagmites grow upon the floor, as the deposit slowly accumulates from the solution which drops from the roof or the tips of stalactites. The Mammoth Cave in Kentucky, the Marengo Cave in Indiana, and the Luray Cavern in Virginia are famous for these fantastic formations. **Mexican onyx** is a variety of stalagmite. Vast deposits of this beautiful mineral are found in Algeria and Mexico. It is translucent and delicately colored, and is used as an ornamental stone, especially for altars, table tops, mantels, soda fountains, and lamp standards. Deposits of limestone are found around many mineral springs. **Travertine** occurs near many springs in Italy. When fresh, it is soft and porous, but it soon hardens and becomes a durable building stone in dry climates. The walls of many ancient buildings in Italy are travertine. Limestone often contains shells and fossils, confirming our belief that limestone is the remains largely of the shells of animals. The calcium carbonate dissolved

in the ocean is transformed by marine organisms into shells and bony skeletons. The hard parts of these animals accumulate in vast quantities on the ocean bottom, become compact, and are finally elevated above the surface of the ocean On certain parts of the coast of Florida, coquina or shell rock is found. It is a mass of fragments of shells cemented by calcium carbonate, and in time it may become compact

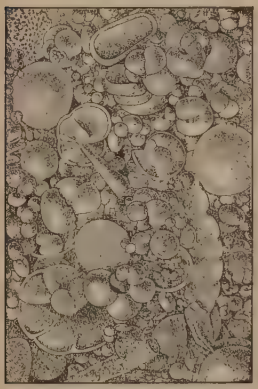


FIG. 72. — Ooze from the ocean bottom, showing globigerina shells (magnified).

FIG. 73. — Globigerina shells (magnified) found in chalk from Iowa.

limestone. **Chalk** is the remains of shells of minute animals. When examined under the microscope, a good specimen is seen to consist almost entirely of tiny shells. The ocean contains myriads of minute animals, and when they die, their shells, which are calcium carbonate, sink to the bottom. As a result, the ocean bottom is partly covered with a gray mud, called globigerina ooze. Under the microscope this ooze has the appearance shown in Figure 72, and when dried and compressed it can hardly be distinguished from chalk.

It is believed that the immense beds of chalk found in England and other places were formed from this ooze. Some varieties of chalk under the microscope closely resemble the ooze (Fig. 73). **Whiting** is a variety of impure chalk; **putty** is a mixture of whiting and oil. **Coral** is calcium carbonate, and the vast accumulations in the sea are the skeletons of the coral animals.

The properties of calcium carbonate, discussed in Chapter XV, may be profitably reviewed by the student at this point.

**Calcium Bicarbonate** or **Acid Calcium Carbonate**, $Ca(HCO_3)_2$ or $H_2Ca(CO_3)_2$, is a salt formed by dissolving calcium carbonate in water containing carbon dioxide. It decomposes readily and deposits the normal carbonate ($CaCO_3$). (See also Stalactites and Hardness of Water.)

**Calcium Oxide**, CaO, is the chemical name of **lime.** It is a porous white solid. Pure lime is almost infusible, and when heated in the oxyhydrogen flame it gives an intensely bright light, sometimes called the "lime light." (See Hydrogen and Calcium Light.) In the electric furnace it melts and volatilizes, if the heating is prolonged. Lime containing impurities, like sand, clay, and iron compounds, melts quite readily into a glass or slag. Exposed to the air, lime becomes "air slaked," that is, it slowly absorbs water and carbon dioxide, swells, and soon crumbles to a powder, which is a mixture of calcium hydroxide and calcium carbonate. When fresh lime and water are mixed, the lime soon becomes warm, swells, and finally liberates considerable heat, as may often be seen when mortar is being prepared. This operation is called "slaking," and the product is "slaked lime." The equation for the chemical change is —

$$\underset{\text{Calcium Oxide}}{CaO} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium Hydroxide}}{Ca(OH)_2}$$

Fresh lime disintegrates organic matter, and is therefore often called "caustic lime" or **quicklime.** It combines with water to form calcium hydroxide and interacts with acids to form calcium salts.

Lime is one of the most useful substances. It is used in preparing mortar, cement, and metals, in making bleaching powder, calcium carbide, and glass, in purifying illuminating gas and sugar, in removing hair from hides before the process of tanning, in dyeing and bleaching cotton cloth, in drying gases, and as a disinfectant and fertilizer.

Lime is prepared on a large scale by heating limestone in a partly closed cavity or vessel. The decomposition takes place according to the equation —

$$\underset{\text{Calcium Carbonate}}{CaCO_3} = \underset{\text{Calcium Oxide}}{CaO} + \underset{\text{Carbon Dioxide}}{CO_2}$$

The carbon dioxide gas escapes, and the lime is left in the kiln.

FIG. 74. — Periodic limekiln (vertical section).

Limestone was formerly "burned" in a cavity on a hillside, and in some regions it is so prepared to-day. This is a crude process and has been largely superseded by well-regulated decomposition in limekilns. The older or periodic kiln is constructed of bricks or of blocks of limestone and loosely filled with pieces of limestone from the arch to the top, as shown in Figure 74. The fire is built at the bottom and burns several days; when the kiln is cool, the lime is removed. These kilns have been largely replaced

by the continuous kiln, constructed so that air can be introduced, the heat regulated, the gases swept out, the charges introduced, and the product removed without extinguishing the fire. One form of continuous kiln is shown in Figure 75. Limestone is introduced at *A* and decomposed by the heat from the gases generated in *B*, *B*. The lime is withdrawn at *C*, *C*. Carbon dioxide and other waste gases escape through the top of the kiln.

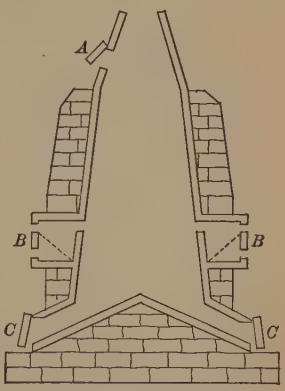



FIG. 75. — Continuous limekiln (vertical section).

Limestone, containing more than 10 per cent of clay, forms **hydraulic lime**, which becomes very hard when wet or kept in contact with water. Cements are varieties of hydraulic lime. They are made by heating a mixture (natural or artificial) of limestone, clay, and sand, and grinding the product to a very fine powder. Rosendale and Portland are the common brands. The hardening of cements is not well understood.

**Soda Lime** is a mixture of lime and sodium hydroxide. It is used in chemical analysis to absorb carbon dioxide and to liberate ammonia from nitrogenous compounds.

**Calcium Hydroxide**, $Ca(OH)_2$, is a white powder. It is sparingly soluble in water, but more soluble in cold than in warm water. The solution has a bitter taste, an alkaline reaction, and is commonly called **limewater**. Exposed to the air, limewater becomes covered with a thin film of calcium carbonate, owing to the interaction of carbon dioxide and calcium hydroxide. For the same reason, limewater

becomes turbid or cloudy when carbon dioxide is passed into it. The formation of calcium carbonate in this way is the usual **test for carbon dioxide.** The equation for this chemical change is —

$$\underset{\text{Calcium Hydroxide}}{Ca(OH)_2} + \underset{\text{Carbon Dioxide}}{CO_2} = \underset{\text{Calcium Carbonate}}{CaCO_3} + H_2O$$

Limewater is prepared by carefully adding lime to considerable water, allowing the mixture to stand for a day or two in a stoppered bottle, and then removing the clear liquid. When considerable calcium hydroxide is suspended in the liquid, the mixture is called **milk of lime.** Ordinary whitewash is thin milk of lime. Limewater is used in the chemical laboratory and as a medicine.

**Mortar** is a thick paste formed by mixing lime, sand, and water. It slowly hardens or "sets," owing to the loss of water and the absorption of carbon dioxide. It hardens without much shrinking, and when placed between bricks or stones holds them firmly in place. The sand makes the mass porous and thus facilitates the change of the hydroxide into the carbonate. The sand is changed chemically only to a very slight extent, if at all. Hair is sometimes added to make the mortar stick better, especially when it is used as **plaster** for walls.

**Calcium Sulphate**, $CaSO_4$. — This salt occurs abundantly and in several varieties. Anhydrite ($CaSO_4$) is associated with sodium chloride. The other varieties are often grouped under the general term *gypsum* and have the composition $CaSO_4 . 2\ H_2O$. Ordinary **gypsum** occurs as white masses and is known as rock or massive gypsum. The lustrous, translucent, crystalline kind is called **selenite** and is very pure; fine-grained masses are named **alabaster**, and the

fibrous varieties are **satin spar.** Most varieties of gypsum are soft, selenite being easily scratched with the finger nail.

Calcium sulphate is slightly soluble in water. When gypsum is heated, it gradually loses its water of crystallization, and becomes opaque (if previously crystalline) and friable. When this dehydrated product is mixed with water, it forms a paste which soon solidifies or "sets" to a white porous mass with a smooth surface. If the raw material is of good quality and the temperature is kept near 125° C., the final product is **plaster of Paris**; it has the composition $(CaSO_4)_2 . H_2O$ and sets quickly owing to the formation of a network of crystals of the less soluble salt ($CaSO_4 . 2 H_2O$). But if the gypsum is impure or the temperature high, the product sets slowly; this variety is called cement plaster. Sometimes a slowly setting plaster is made by adding a retarder such as alum or borax during or after the calcination. Many kinds of plaster are made from gypsum and their names are applied rather indefinitely.

Plaster of Paris expands slightly in setting and is therefore used to make exact reproduction of statues and ornaments; considerable is used in making molds and in cementing glass to metal. Alabaster, being soft and beautiful in texture, is carved into statues and ornaments. Many grades of calcined gypsum are used as a coating for walls and as the principal ingredient of fine plasters. Crude gypsum is used in the manufacture of glass and porcelain; pulverized gypsum is used as a fertilizer under the name of land plaster. **Stucco** is a mixture of plaster of Paris and glue.

**Calcium Chloride**, $CaCl_2$, is a white solid. It absorbs moisture rapidly and is used to dry many gases, not only in the laboratory, but also in such industrial processes as the manufacture of carbon dioxide. The crystallized variety dissolves readily in water, and the solution is attended by a marked

fall of temperature. A mixture of crystallized calcium chloride and snow produces a temperature of $-40°$ C.

The low freezing point of calcium chloride solutions has led to their use in refrigerating plants and in automatic sprinkler systems. The liquid left from the interaction of calcium carbonate and hydrochloric acid contains calcium chloride, which on concentration is deposited in large crystals. These readily absorb water, but lose their own water of crystallization when heated above 200° C. This anhydrous calcium chloride is porous and is the form usually used as a drying agent. At a high temperature it melts, and solidifies in cooling to a hard mass known as fused calcium chloride.

Calcium chloride is found in small quantities in some of the Stassfurt salts. It is obtained in large quantities as a by-product in the manufacture of sodium carbonate (by the Solvay process) and other chemicals.

**Compounds of Calcium.** — Many compounds of calcium have already been discussed and may be reviewed by the student at this point. They are calcium fluoride, calcium carbide, the calcium phosphates, and calcium hypochlorite. **Calcium sulphide** (CaS) is formed by heating a mixture of gypsum and carbon; like other sulphides, it stains silver brown. **Calcium oxalate** ($CaC_2O_4$) is a white solid formed by the interaction of ammonium oxalate and any soluble calcium compound; it is insoluble in acetic acid but soluble in hydrochloric acid. Its formation and properties serve as a **test for calcium compounds**. Another test is the yellow-red color imparted to the Bunsen flame by calcium compounds, especially the chloride. The spectrum of calcium is characterized by a red and a green line.

Calcium compounds in aqueous solution yield colorless calcium ions ($Ca^{++}$). The atomic weight of calcium is 40.09, and its valence is two.

**Calcium Compounds and Hardness of Water.** — Calcium sulphate is slightly soluble in water, and calcium carbonate, as we have already seen, is changed into the soluble, unstable acid carbonate by water containing carbon dioxide. Water having these salts of calcium in solution is called **hard water.** They form sticky, insoluble compounds with soap, and as long as water contains such salts, the soap is useless as a cleansing agent. Heat decomposes acid calcium carbonate, and the hardness due to calcium carbonate is called **temporary hardness**, because boiling removes it; temporary hardness can also be removed by the addition of a little slaked lime. The hardness caused by calcium sulphate cannot be removed by boiling and is called **permanent hardness.** Magnesium sulphate, like calcium sulphate, also produces permanent hardness. Permanent hardness can be removed, however, by adding sodium carbonate to the water, because the calcium sulphate and sodium carbonate interact and produce soluble sodium sulphate and insoluble calcium carbonate; the latter can be removed by filtering or by allowing the mixture to stand and then drawing off the supernatant water. When hard water is used in steam boilers, the calcium salts are often deposited as a hard mass known as "boiler scale." Soft water, such as rain water, contains little or no calcium or magnesium salts.

## Strontium and Barium

**Strontium**, Sr, and **Barium**, Ba, are uncommon metallic elements. They resemble calcium closely in their physical and chemical properties. The metals themselves never occur free, and are hardly more than chemical curiosities. Their compounds are abundant, and some are useful.

**Compounds of Strontium.** — The native compounds are the beautifully crystalline minerals, strontianite (strontium

carbonate, $SrCO_3$) and celestite (strontium sulphate, $SrSO_4$). **Strontium oxide** (strontia, SrO), like lime, is made by heating the carbonate. It unites with water to form **strontium hydroxide** ($Sr(OH)_2$), which is used in the manufacture of beet sugar. **Strontium nitrate** ($Sr(NO_3)_2$) and other salts of strontium color a flame crimson, and are widely used in making fireworks, especially "red fire." The latter is a mixture of potassium chlorate, shellac, and strontium nitrate. Several strontium salts are used as medicines.

The crimson color imparted to the Bunsen flame is the usual **test for strontium**. The spectrum of strontium is characterized by several red lines and a blue one.

**Compounds of Barium.** — The most abundant native compounds are witherite (barium carbonate, $BaCO_3$) and barite (barium sulphate, heavy spar, barytes, $BaSO_4$). The **oxides**, BaO and $BaO_2$, have already been mentioned as a source of oxygen. **Barium hydroxide** ($Ba(OH)_2$) solution is often called **baryta water**, and it forms insoluble barium carbonate ($BaCO_3$) by interaction with carbon dioxide. **Barium chloride** ($BaCl_2$) is a white crystalline solid; it is used in the laboratory to test for sulphuric acid and soluble sulphates, because it readily interacts with them and forms insoluble **barium sulphate** ($BaSO_4$). The latter salt is a fine white powder, and being cheap and heavy it is a common adulterant of ordinary white paint. Ground native barium sulphate has a similar use. Barium sulphate is also used to increase the weight of paper and to give it a gloss. Barium salts color a flame green, and **barium nitrate** ($Ba(NO_3)_2$) is extensively used in making fireworks, especially "green fire." Commercial **barium sulphide** (BaS), as well as the sulphides of calcium and strontium, shine feebly in the dark, after having been exposed to a bright light. On account of this property they are used in making luminous paint. **Barium**

**chromate** ($BaCrO_4$) is a yellow solid obtained by the interaction of a soluble barium compound and potassium dichromate. Soluble barium salts, unlike those of calcium, are poisonous.

The green color imparted to the Bunsen flame is the **test for barium.** The spectrum of barium is characterized by several green and orange lines.

Aqueous solutions of strontium and of barium compounds contain colorless strontium ions ($Sr^{++}$) and barium ions ($Ba^{++}$).

**The Alkaline Earth Family.** — This is a typical family and resembles its contiguous families, the alkali metals and the earth metals. The metals themselves, if calcium is taken as a type, are less active than sodium and potassium but more active than aluminium. Not only have these elements properties which are much alike, but they also show a gradation in properties as the atomic weight increases. All interact with cold water, burn in air, and form analogous compounds whose properties are strikingly suggestive of family relationship; on the other hand their densities increase from about 1.5 for calcium (at. wt. 40.09) through 2.5 for strontium (at. wt. 87.62) to 3.57 for barium (at. wt. 137.37). All three elements form an hydroxide, a carbonate, a nitrate, and a sulphate. The solubility of the chlorides and nitrates is quite marked and decreases in the order in which the metals have been studied (calcium, strontium, barium); the hydroxides are much less soluble and in the opposite order; while the sulphates vary widely in solubility, a liter of water dissolving about 2 gm. of calcium sulphate and only .0023 gm. of barium sulphate. All the compounds of these elements are white, except barium chromate, which is yellow. The valence of the alkaline earth elements in their compounds is almost invariably two.

### Problems and Exercises

1. What is the per cent of calcium in (*a*) marble ($CaCO_3$), (*b*) gypsum ($CaSO_4 . 2\ H_2O$), (*c*) fluor spar ($CaF_2$), (*d*) superphosphate of lime ($CaH_4(PO_4)_2$)?

2. How many tons of limestone must be heated to produce 100 tons of quicklime? (Assume $CaCO_3 = CaO + CO_2$.)

3. Calculate the simplest formula of a compound having the percentage composition Ca = 40, C = 12, O = 48.

4. Suppose 9.00246 gm. of calcium chloride interact with silver nitrate and form 23.2506 gm. of silver chloride. Accepting 107.88 and 35.45 as the atomic weights of silver and chlorine respectively, what is the atomic weight of calcium?

5. Write the formulas of the following compounds by applying the principle of valence (Chapter XIV): Acid calcium phosphate, calcium nitrate, calcium iodide, calcium bromide, strontium chloride, strontium oxide, barium sulphide, barium monoxide, barium chlorate, calcium phosphate (ortho), strontium sulphide.

6. Write the equation for the reaction between barium chloride and sulphuric acid in (*a*) the ordinary chemical form and (*b*) the ionic form.

## Radium

**Radium**, Ra, is an element related to barium. Its compounds are obtained by a tedious process from certain rare minerals containing uranium, chiefly the mineral pitchblende. The proportion of radium in pitchblende is exceedingly minute, a few milligrams to the ton.

Metallic radium has recently been isolated, and several compounds, especially radium chloride ($RaCl_2$) and radium bromide ($RaBr_2$), have been prepared and studied. Radium compounds color the Bunsen flame red, have a different spectrum from other elements, are naturally phosphorescent, and produce phosphorescence in various substances, *e.g.* barium platino-cyanide ($BaPt(CN)_4$), diamond, willemite, and zinc sulphide. Besides the properties just mentioned, radium compounds have others which are conspicuously

different from those exhibited by most substances. Thus, they spontaneously evolve relatively large quantities of heat, affect a photographic plate, and discharge an electroscope. They also undergo and produce remarkable chemical changes. These properties are called radio-active properties. Similar ones are possessed by uranium, thorium, and other substances; and radio-activity can be more appropriately discussed under these elements. (See Chapter XXXII.)

The general properties of radium indicate that it belongs to the alkaline earth family. Its atomic weight is 226.4, and its valence is two.

# CHAPTER XXVIII

## Magnesium, Zinc, Cadmium, and Mercury

These elements form a natural family in Group II of the periodic classification, though the members are not as closely related as in the alkali and alkaline earth families.

### Magnesium

**Occurrence of Magnesium.** — Magnesium is never found free. In combination it is widely distributed and very abundant, constituting about 2.5 per cent of the earth's crust. Dolomite is magnesium calcium carbonate ($CaCO_3 . MgCO_3$ or $CaMg(CO_3)_2$); it forms whole mountain ranges in the Tyrol and vast deposits in many regions. Dolomite resembles marble and limestone in its properties. Magnesium carbonate ($MgCO_3$) is also abundant. Many of the Stassfurt salts contain magnesium, for example, kainite ($KCl, MgSO_4 . 3\,H_2O$), carnallite ($KCl, MgCl_2 . 6\,H_2O$), and kieserite ($MgSO_4 . H_2O$). Magnesium is a component of serpentine, talc, soapstone, asbestos, meerschaum, and other silicates. The sulphate ($MgSO_4$) and chloride ($MgCl_2$) are found in sea water and in mineral springs.

**Preparation of Magnesium.** — Magnesium was formerly prepared by reducing the chloride with sodium. It is now economically manufactured by the electrolysis of fused carnallite. A sketch of the essential parts of the apparatus is shown in Figure 76. Carnallite is put into the cylindrical iron vessel *C*, which is the cathode. This is closed by the

air-tight cover through which pass the pipes $D$, $D'$ for conveying inert gases into and out of the apparatus. The carbon anode $A$ dips into the carnallite and is inclosed by the porcelain cylinder $B$, which is provided with a pipe $E$, for the escape of the chlorine liberated at the anode. The carnallite is kept fused by external heat. When the current passes, the chlorine liberated at the anode escapes through $E$, and the magnesium liberated at the cathode floats on the fused carnallite and is prevented from oxidizing by the inert gas supplied through $D$. The porcelain cylinder $B$ prevents the chlorine from escaping into the larger vessel. The molten magnesium is carefully removed at intervals.

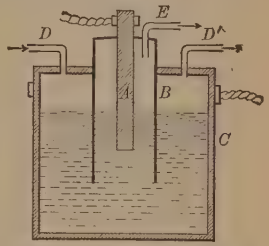



FIG. 76. — Apparatus for the manufacture of magnesium by the electrolysis of carnallite.

**Properties of Magnesium.** — Magnesium is a lustrous, silvery white metal. It is a light metal, the specific gravity being only about 1.75. It is tenacious and ductile, and when hot can be drawn into wire or pressed into ribbon, the latter being a common commercial form. It melts at about 633° C. and can be cast into different shapes. At a higher temperature it volatilizes. It is easily kindled by a match or candle, and burns with a dazzling light, producing dense white clouds of magnesium oxide (MgO). It does not tarnish in dry air, but in moist air it is soon covered with a film of oxide. It liberates hydrogen from acids and from boiling water. Heated in nitrogen, it forms magnesium nitride ($Mg_3N_2$).

**Uses of Magnesium.** — Magnesium in the form of powder is used chiefly in taking flash-light photographs. Small

quantities are used in making fireworks. The powder and ribbon are used in the chemical laboratory as a convenient form of the metal. Some is used to reduce rare metals from their oxides.

**Magnesium Oxide**, MgO, is a white, bulky powder. It is formed when magnesium burns in the air, but it is manufactured by gently heating magnesite ($MgCO_3$), just as lime is made from limestone. It is often called **magnesia**, or calcined magnesia. The native oxide is the mineral periclase. Magnesia dissolves very slightly in water, forming **magnesium hydroxide** ($Mg(OH)_2$). A mixture of magnesia and water, with or without magnesium chloride, hardens on exposure to the air, and is sometimes used as a cement or artificial stone. Native magnesium hydroxide is the mineral brucite. Like lime, magnesia withstands a high temperature, and is, therefore, used as the lining of electrothermal apparatus, metallurgical furnaces, and cement kilns, and as the chief ingredient of a protective covering for steam pipes. Magnesia is used in medicine as a mild alkali and as an antidote for poisoning by mineral acids.

**Magnesium Sulphate**, $MgSO_4$, is a white solid. There are several crystalline varieties. The native salt kieserite ($MgSO_4 . H_2O$), when added to water, changes into **Epsom salts** ($MgSO_4 . 7\,H_2O$). This variety was first found in the mineral spring at Epsom, England. It is efflorescent, very soluble in water, and its solution has a bitter taste. It is used in medicine as a purgative, in manufacturing sulphates of sodium and potassium, as a fertilizer in place of gypsum, and as a coating for cotton cloth.

**Magnesium Chloride**, $MgCl_2$, is a white solid. It is a by-product in the preparation of potassium chloride. The crystallized salt ($MgCl_2 . 6\,H_2O$) is very deliquescent. Magnesia mixture is a mixture of magnesium chloride, ammonium

chloride, and ammonium hydroxide; it is used in chemical analysis to detect and determine orthophosphates.

**Magnesium Carbonate**, $MgCO_3$, occurs native as **magnesite**, and combined with calcium carbonate as **dolomite**. Magnesite is converted by heat into magnesia and carbon dioxide; the magnesia, as stated above, is very generally used as a refractory material, while the gas is utilized in the preparation of liquid carbon dioxide or of charged beverages. The commercial salt known as magnesia alba, or simply magnesia, is a basic carbonate (approximately $Mg_4(OH)_2(CO_3)_3$). Many face powders consist chiefly of magnesia alba.

It was during an investigation of magnesia alba that Black (1728–1799) discovered carbon dioxide and showed the close relation between analogous compounds of magnesium and calcium.

**Miscellaneous.** — Besides the oxide and sulphate other magnesium compounds are used as medicines. **Fluid magnesia** is prepared by dissolving magnesium carbonate in water containing carbon dioxide or by suspending magnesium hydroxide in water; it is a mild alkali and laxative. **Magnesium citrate** has a similar action; it is an effervescing mixture prepared from sodium bicarbonate, tartaric and citric acids, sugar, and magnesium sulphate. When disodium phosphate and ammonium hydroxide are added to the solution of a magnesium compound, a white crystalline precipitate of **ammonium magnesium phosphate** ($NH_4MgPO_4$) is produced; its formation is a **test for magnesium**. Another test (though often indifferent) is the pale pink residue left after a magnesium compound has been intensely heated in a blowpipe flame and subsequently moistened with cobaltous nitrate solution.

Soluble magnesium compounds yield colorless magnesium ions ($Mg^{++}$). The atomic weight of magnesium is 24.32, and the valence is two.

## Zinc

**Occurrence of Zinc.** — Free zinc is never found. The ores of zinc are not numerous, though rather abundant. The chief ores are the sulphide (sphalerite or zinc blende, ZnS), the carbonate (smithsonite, $ZnCO_3$), the silicate (calamine, $H_2Zn_2SiO_5$), and the red oxide (zincite, ZnO). Franklinite ($Zn(FeO_2)_2$) and willemite ($Zn_2SiO_4$) are complex ores which also contain manganese and iron. Gahnite has the composition $ZnAl_2O_4$.

Zinc ores are found in Germany, Italy, France, Greece, Austria-Hungary, Belgium, England, and the United States. Missouri and Kansas contain large deposits of the sulphide, while the other ores occur chiefly in New Jersey.

**Metallurgy of Zinc.** — Zinc is easily smelted. The ores are first roasted to change them into the oxide, thus: —

$$\underset{\text{Zinc Carbonate}}{ZnCO_3} = \underset{\text{Zinc Oxide}}{ZnO} + \underset{\text{Carbon Dioxide}}{CO_2}$$

$$\underset{\text{Zinc Sulphide}}{2\,ZnS} + \underset{\text{Oxygen}}{3\,O_2} = \underset{\text{Zinc Oxide}}{2\,ZnO} + \underset{\text{Sulphur Dioxide}}{2\,SO_2}$$

The oxide is then reduced by heating it with coal. This operation is conducted in fire-clay retorts connected with iron or clay receivers into which the vapor passes; at first it condenses as a blue-gray powder known as zinc dust, which is really a mixture of zinc and zinc oxide; but it finally condenses as a liquid, which is drawn off at intervals and cast into bars or plates. The impure, massive zinc thus obtained is called **spelter**; it is freed from carbon, lead, iron, cadmium, and arsenic by repeated distillation, often under reduced pressure.

**Properties of Zinc.** — Zinc is a bluish white, lustrous metal. Its physical properties vary with the temperature. At or-

dinary temperatures it is brittle, but at 120°–150° C. it is soft and can be rolled into sheets and drawn into wire, while its specific gravity rises from 6.9 to 7.2. Zinc which has been rolled or drawn does not become brittle upon cooling, but remains pliable. At 200° C. it again becomes brittle and can be easily pulverized. It melts at about 420° C. and boils at about 920° C. Heated in the air above its melting point, zinc burns with a bluish green flame, forming white zinc oxide (ZnO). Zinc does not tarnish in dry air, but in moist air it slowly becomes coated with a hard, coherent film which prevents further action. With hot solutions of sodium and potassium hydroxides, it forms zincates and liberates hydrogen, thus: —

$$\underset{\text{Potassium Hydroxide}}{2\,KOH} + \underset{\text{Zinc}}{Zn} = \underset{\text{Hydrogen}}{H_2} + \underset{\text{Potassium Zincate}}{K_2ZnO_2}$$

Commercial zinc interacts with dilute acids and liberates hydrogen (except from nitric acid). Pure zinc interacts with acids if in contact with platinum, iron, or copper, or if copper sulphate is added to the mixture. Zinc displaces many other metals (*e.g.* lead, tin, copper, and mercury) from their solutions; it is strongly electropositive. (See Displacement of Metals, Chapter XXVI.)

The vapor density of zinc requires the molecular weight 66 (approximately). Since the atomic weight is 65.37, a molecule of zinc vapor contains only one atom.

**Uses of Zinc.** — Zinc in the form of sticks and plates is extensively used as the positive electrode in electric batteries. Sheet zinc is used as a lining for tanks, and as a protective covering which is often placed behind and beneath stoves. Iron dipped into zinc becomes coated with zinc and is called galvanized iron; it does not rust easily, and is often used in place of zinc for roofs, pipes, cornices, and water tanks

Telegraph wire is also galvanized. Zinc dust is sometimes used in the cyanide process of extracting gold and in many chemical experiments in the laboratory. Brass, German silver, and other alloys contain zinc. (See Alloys of Copper.) Antifriction metals, which are used for bearings, are alloys of zinc; Babbitt's metal, for example, contains approximately 69 per cent of zinc, 19 of tin, 4 of copper, 3 of antimony, and 5 of lead.

**Compounds of Zinc.** — Native **zinc oxide** (ZnO) is red, owing to the presence of manganese, but the pure oxide is white when cold and yellow when hot. It is formed when zinc burns, and is manufactured in this way or by heating zinc carbonate. It is often called "zinc white" or "Chinese white," and is used to make a white paint which is not discolored by sulphur compounds (especially hydrogen sulphide), and is therefore well suited for painting the walls of a chemical laboratory. It is also used as an ingredient of ointments and cosmetics. Native **zinc sulphide** (ZnS) is yellow, brown, or black on account of impurities, but the pure sulphide is white. The latter is formed as a jellylike precipitate when hydrogen sulphide is passed into an alkaline solution of a zinc salt; it is decomposed by a mineral acid (*e.g.* HCl). Zinc sulphide is also used as a white pigment. **Zinc sulphate** ($ZnSO_4$) is formed by the interaction of zinc and dilute sulphuric acid. Large quantities are made by roasting the sulphide in a limited supply of oxygen and extracting the sulphate with water. It is a white, crystalline solid ($ZnSO_4 . 7\ H_2O$), which effloresces in the air, and when heated to 100° C. loses most of its water of crystallization. The crystallized salt is called white vitriol. It is used in dyeing and calico printing, as a disinfectant, and as a medicine. It is poisonous, but can be safely used externally to relieve inflammation. **Zinc chloride** ($ZnCl_2$) is a white, deliquescent

solid, prepared by dissolving zinc in hydrochloric acid and evaporating the solution until a sample solidifies on cooling. It is used in surgery, and also as a constituent of a mixture for filling teeth; large quantities are used to preserve wood, especially railroad ties, from decay, nearly 1500 tons being annually consumed for this purpose. **Zinc hydroxide** ($Zn(OH)_2$) is formed as a dull white, flocculent precipitate by the interaction of sodium or potassium hydroxide and the solution of a zinc salt, thus: —

$$\underset{\text{Zinc Sulphate}}{ZnSO_4} + \underset{\text{Sodium Hydroxide}}{2\,NaOH} = \underset{\text{Zinc Hydroxide}}{Zn(OH)_2} + \underset{\text{Sodium Sulphate}}{Na_2SO_4}$$

An excess of the alkaline hydroxide changes the zinc hydroxide into a soluble **zincate**, thus: —

$$\underset{\text{Zinc Hydroxide}}{Zn(OH)_2} + \underset{\text{Sodium Hydroxide}}{2\,NaOH} = \underset{\text{Sodium Zincate}}{Na_2ZnO_2} + \underset{\text{Water}}{2\,H_2O}$$

Zinc salts are poisonous.

**Tests for Zinc.** — The formation of the sulphide or the hydroxide and a soluble zincate as above described serves as the **test for zinc.** A green incrustation is produced when zinc compounds are heated on charcoal and then moistened with a cobaltous nitrate ($Co(NO_3)_2$) solution.

**Miscellaneous.** — Zinc acts as a metal and a non-metal. Thus, in compounds like zinc sulphate, zinc chloride, and zinc sulphide it is a metal; solutions of the class contain colorless zinc ions ($Zn^{++}$). In the zincates, such as sodium zincate ($Na_2ZnO_2$), the zinc acts as a non-metal. Zinc forms complex compounds, *e.g.* with ammonium hydroxide it yields $Zn(NH_3)_4(OH)_2$. In solutions of complex zinc compounds, the zinc is often a part of a complex ion.

The valence of zinc is two.

## Cadmium

**Cadmium**, Cd, is an uncommon metal; certain compounds are frequently found in zinc and other ores. It also occurs as a **sulphide** (greenockite, CdS). It is white, lustrous, and rather soft. Its specific gravity is about 8.6 and its melting point is about 320° C. Cadmium is a constituent of certain dental amalgams and fusible alloys. (See Bismuth.) Wood's metal contains 12 per cent of cadmium.

The most important compound is **cadmium sulphide** (CdS). This is a bright yellow solid, formed by adding hydrogen sulphide to the solution of a cadmium compound. It is used as a pigment. Its formation also serves as a **test for cadmium**. Warm dilute sulphuric acid dissolves cadmium sulphide owing to the formation of soluble cadmium sulphate, but cadmium sulphide does not dissolve in potassium cyanide solution; both operations permit the more or less complete separation of cadmium and copper compounds. **Cadmium hydroxide** ($Cd(OH)_2$) is a white solid formed upon the addition of sodium hydroxide to the solution of a cadmium compound; it is insoluble in an excess of sodium hydroxide but soluble in an excess of ammonium hydroxide.

Cadmium has a valence of two in all its compounds. Its vapor density requires the molecular weight 112 (approximately). Since the atomic weight is 112.4, a molecule of the vapor contains one atom.

Aqueous solutions of cadmium compounds contain colorless cadmium ions ($Cd^{++}$). The element also forms complex ions, *e.g.* $Cd(NH_3)_4^{++}$ and $Cd(CN)_4^{--}$.

## Mercury

**Occurrence of Mercury.** — Native mercury is occasionally found in minute globules, but the most abundant ore is mercuric sulphide (cinnabar, HgS). The ore is mined in

Spain, Austria, Russia, Italy, and Mexico; in the United States large quantities are obtained in California and Texas.

Mercury has been known for ages as quicksilver. The Latin name, *hydrargyrum*, which gives the symbol Hg, means literally, "water silver," emphasizing the fact, so well known, that mercury looks like silver and flows like water.

**Preparation of Mercury.** — Mercury is prepared by roasting cinnabar in an open furnace or closed retort. In the furnace the sulphide is transformed by the oxygen of the air into mercury and sulphur dioxide, thus: —

$$\underset{\text{Cinnabar}}{HgS} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Mercury}}{Hg} + \underset{\text{Sulphur Dioxide}}{SO_2}$$

In the retort lime is mixed with the ore and the equation for the reaction is: —

$$\underset{\text{Mercuric Sulphide}}{4\,HgS} + \underset{\text{Lime}}{4\,CaO} = \underset{\text{Mercury}}{4\,Hg} + \underset{\text{Calcium Sulphide}}{3\,CaS} + \underset{\text{Calcium Sulphate}}{CaSO_4}$$

In each process the mercury is liberated as a vapor and condensed in a series of cooled chambers. The crude mercury is freed from soot and dust and collected into large globules by stirring and rubbing; it is farther purified by filtering it through charcoal or chamois skin. Metallic impurities are removed by distillation or by agitation with dilute nitric acid. Mercury is sent into commerce in strong iron flasks, holding about 75 pounds.

**Properties of Mercury.** — Mercury is a bright, silvery metal, and is the only one which is liquid at ordinary temperatures. It solidifies at about $-39.5°$ C., and boils at about $357°$ C. It is a heavy metal, the specific gravity being about 13.59. It is slightly volatile even at ordinary temperatures, and the vapor is poisonous. Mercury does not tarnish in the air,

unless sulphur compounds are present. At a high temperature it combines slowly with oxygen to form the red oxide (HgO). Hydrochloric acid and cold sulphuric acid do not affect it; hot concentrated sulphuric acid oxidizes it, and nitric acid changes it into nitrates.

The vapor density of mercury requires the molecular weight 200 (approximately). Since the atomic weight is 200, a molecule of the vapor contains only one atom.

**Uses of Mercury.** — Mercury is used in making thermometers, barometers, manometers, and many other kinds of scientific apparatus. Its extensive use in extracting gold and silver has been mentioned. (See Amalgamation.) Considerable is used in preparing amalgams, medicines, and explosives (*e.g.* fulminating mercury, which is used in percussion caps and cartridges). It has also come into use recently as an electrode in various electrochemical processes.

**Amalgams** are alloys of mercury with other metals. They are easily prepared by mixing the constituents. Sometimes the union is violent, as in the preparation of **sodium amalgam.** Amalgamated zinc is usually used in electric batteries to prevent unnecessary loss of the zinc. Tin amalgam is sometimes used to coat mirrors. Amalgams of certain metals are used as a filling for teeth. Care should be taken, while handling mercury, not to let it come in contact with gold rings, since gold amalgam is readily formed. Iron is the only common metal which does not form an amalgam.

**Compounds of Mercury.** — Mercury, like copper, forms two classes of compounds — the mercurous and the mercuric. The valence of mercury is one in the mercurous compounds and two in the mercuric. **Mercuric oxide** (HgO) is a red powder, produced by heating mercury in air or by heating a mixture of mercury and mercuric nitrate. As we have

already seen, mercuric oxide is decomposed by heat into mercury and oxygen. A yellow variety is produced by the interaction of sodium hydroxide and a mercuric salt, thus: —

$$\underset{\text{Sodium Hydroxide}}{2\,NaOH} + \underset{\text{Mercuric Nitrate}}{Hg(NO_3)_2} = \underset{\text{Mercuric Oxide}}{HgO} + \underset{\text{Sodium Nitrate}}{2\,NaNO_3} + \underset{\text{Water}}{H_2O}$$

**Mercurous chloride** ($Hg_2Cl_2$ or HgCl) is a white, tasteless powder, insoluble in water. It is formed when a chloride and mercurous nitrate interact, but it is manufactured usually by heating a mixture of mercuric chloride and mercury. Under the name of **calomel** it is extensively used as a medicine. **Mercuric chloride** ($HgCl_2$) is a white, crystalline solid, soluble in water and in alcohol. It is prepared by heating a mixture of mercuric sulphate and common salt. *It is a violent poison.* The best antidote is the white of a raw egg. The albumen forms an insoluble mass with the poison, which can then be removed from the stomach. The common name of mercuric chloride is **corrosive sublimate**. It has strong antiseptic properties and is extensively used in surgery to protect wounds from the harmful action of germs; taxidermists sometimes use it to preserve skins, and it has many serviceable applications as a medicine and disinfectant. It is usually used as a dilute solution (1 part to 1000 parts of water). Native **mercuric sulphide** or cinnabar (HgS) is a red crystalline solid. When hydrogen sulphide is passed into a solution of a mercuric salt, mercuric sulphide is formed as a black precipitate; this variety, when heated, changes into red crystals. **Vermilion** is artificial mercuric sulphide. It is manufactured either (1) by grinding together mercury and sulphur and treating this mass with potassium hydroxide, or (2) by heating mercury and sulphur in iron pans and subliming the black mass. In both processes the product must be carefully ground, washed, and dried.

Chinese vermilion is the best quality. Vermilion has a brilliant red color, and, although expensive, is widely used to make red paint. **Mercurous nitrate** ($HgNO_3$ or $Hg_2(NO_3)_2$) and **mercuric nitrate** ($Hg(NO_3)_2$) are prepared by treating mercury respectively with cold dilute nitric acid and warm concentrated nitric acid. They are white, crystalline solids.

Soluble mercurous compounds yield mercurous ions ($Hg^+$) and mercuric compounds mercuric ions ($Hg^{++}$). Both kinds are colorless. Mercury also forms complex ions, *e.g.* $Hg(CN)_4^{--}$.

**Tests for Mercury.** — Clean copper becomes coated with a bright film of mercury when put into the solution of any mercury compound. Other metals act similarly. (See Displacement of Metals, Chapter XXVI.) Hydrochloric acid precipitates white mercurous chloride from solutions of mercurous salts. Stannous chloride in excess produces with mercuric salts at first white mercurous chloride and finally a gray precipitate of finely divided mercury, thus : —

$$\underset{\text{Mercuric Chloride}}{2\,HgCl_2} + \underset{\text{Stannous Chloride}}{SnCl_2} = \underset{\text{Mercurous Chloride}}{2\,HgCl} + \underset{\text{Stannic Chloride}}{SnCl_4}$$

$$\underset{\text{Mercurous Chloride}}{2\,HgCl} + \underset{\text{Stannous Chloride}}{SnCl_2} = \underset{\text{Mercury}}{2\,Hg} + \underset{\text{Stannic Chloride}}{SnCl_4}$$

This is a typical illustration of the broad use of the terms "oxidation" and "reduction," viz. the addition and removal of a negative element. In these two chemical changes the stannous chloride is oxidized to stannic chloride, *i.e.* the negative element chlorine is added chemically to stannous chloride. On the other hand, mercuric and mercurous chloride both lose chlorine, becoming respectively mercurous chloride and mercury, *i.e.* the negative element chlorine is removed chemically from the two mercury compounds.

Mercurous salts yield a black precipitate with ammonium hydroxide, while mercuric salts yield a white one. These products are complex mercury-ammonia compounds, *e.g.* $HgNH_2Cl$.

**The Zinc Family.** — The four elements just considered (together with beryllium) constitute a natural family in the periodic classification. They bear certain resemblances to the calcium family, which is in the same periodic group, and the different members resemble each other; but the family is not a unit, nor does it exhibit the progressive change in properties which characterizes certain families. Zinc and cadmium are much alike, while mercury differs somewhat from these metals and resembles copper. As already stated these metals have the valence two, except mercury, whose valence is one in mercurous compounds and two in mercuric compounds.

### Problems and Exercises

1. How much magnesium will be formed by heating 100 gm. of potassium with magnesium chloride? (Assume $2\,K + MgCl_2 = Mg + 2KCl$.)

2. What is the per cent of magnesium in (*a*) magnesite ($MgCO_3$), (*b*) dolomite ($MgCa(CO_3)_2$), (*c*) Epsom salts ($MgSO_4.7\,H_2O$)?

3. What is the per cent of zinc in (*a*) zinc sulphate ($ZnSO_4$), (*b*) zinc sulphide (ZnS), (*c*) zinc chloride ($ZnCl_2$), (*d*) zinc oxide (ZnO)?

4. How much zinc sulphate can be prepared from 65 gm. of zinc? from 130 gm.? from 720 gm.?

5. How much mercury is formed by decomposing 400 gm. of cinnabar? (Assume $HgS + O_2 = Hg + SO_2$.)

6. What is the per cent of mercury in (*a*) mercuric oxide (HgO), (*b*) calomel (HgCl), (*c*) corrosive sublimate ($HgCl_2$)?

7. What is the approximate specific heat of cadmium, accepting 112 as its atomic weight?

8. If 64.2501 gm. of cadmium sulphate yield 44.4491 gm. of cadmium sulphide, what is the atomic weight of cadmium (assuming O = 16 and S = 32.07)?

9. If 380.5744 gm. of mercuric oxide yield 352.4079 gm. of mercury, what is the atomic weight of this element?

10. Write the formulas of the following compounds by applying the principle of valence and utilizing analogous formulas in this chapter: Magnesium iodide, ammonium magnesium phosphate, magnesium fluoride, magnesium silicate, potassium zincate, zinc acetate, zinc iodide, cadmium iodide, cadmium sulphate, mercurous bromide, mercuric iodide, mercuric sulphate.

11. What volume of mercury is needed to fill one of the commercial flasks holding 75 pounds?

12. The freezing point of mercury is — 39.5° C. and the boiling point is 357° C. What are the corresponding Fahrenheit temperatures?

13. Give the name and formula of each magnesium double salt found at Stassfurt and indicate the ions found in a dilute aqueous solution of each. (Suggestion — see under Potassium.)

14. Cadmium chloride and hydrosulphuric acid ($H_2S$) form cadmium sulphide and hydrochloric acid. Write (*a*) the ordinary chemical equation, and (*b*) the ionic equation.

15. Calculate the percentage composition of mercurous and mercuric chloride and restate the percentages in a form which illustrates the law of multiple proportions.

# CHAPTER XXIX

## Aluminium

**Occurrence.** — Aluminium (or aluminum), Al, does not occur free in nature, but its compounds are numerous and widely distributed. About 8 per cent of the earth's crust is aluminium. It is the most abundant metal and the third element in abundance in the earth's crust. Many common rocks are silicates of aluminium and other metals, *e.g.* feldspar and mica, which make up a large part of granite and gneiss. Clay and slate are mainly silicate of aluminium, and are formed by the decomposition of complex aluminium minerals. Corundum and emery are more or less impure aluminium oxide ($Al_2O_3$). Bauxite is an impure hydroxide of aluminium ($Al_2O_5H_4$). Cryolite is a fluoride of aluminium and sodium ($Na_3AlF_6$).

**Metallurgy.** — Aluminium is obtained from its purified oxide ($Al_2O_3$) by electrolysis. An open iron vessel lined with carbon is made the cathode (Fig. 77). The anode consists of several carbon bars hung from a common copper rod, which can be lowered as the carbon is consumed. The bottom of the box is first covered with cryolite, the anode is lowered, and the box is then filled with cryolite. The current is turned on, and in its resisted passage through the cryolite enough heat is generated to melt the cryolite. Pure, dry aluminium oxide is now added, which is decomposed into aluminium and oxygen. The oxygen goes to the anode and unites with the carbon, forming carbon monoxide, which burns or escapes. The molten aluminium, which goes to the

cathode, gradually collects on the bottom of the cell. The process is continuous, fresh aluminium oxide being added and the molten aluminium being drawn off at intervals. The cryolite is unchanged chemically.

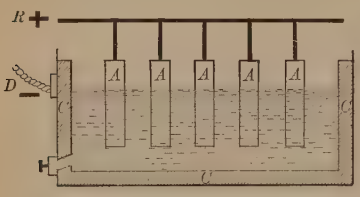



FIG. 77.—Apparatus for the manufacture of aluminium by the electrolysis of aluminium oxide. *C, C, C* is the iron box lined with carbon which serves as a cathode. *A, A*, etc., are carbon bars attached to the copper rod *R*. Connection is made with the cathode at *D*.

**Properties.**—Aluminium is a lustrous, bluish white metal. It is very light compared with other common metals, since its specific gravity is only about 2.6; this value is one third that of iron. It is ductile and malleable, and is often sold in the form of wire and sheets; it must be annealed frequently during the hammering or drawing. It is a good conductor of heat and electricity. Its tensile strength is about as great as that of cast iron. It melts at about 660° C. and can be cast and welded, but not readily soldered so as to produce a permanent joint. Pure aluminium is only very slightly oxidized by air. Hydrochloric acid interacts readily with it, forming aluminium chloride and hydrogen, thus: —

| $2\,Al$ | + | $6\,HCl$ | = | $2\,AlCl_3$ | + | $3\,H_2$ |
|---|---|---|---|---|---|---|
| Aluminium | | Hydrochloric Acid | | Aluminium Chloride | | Hydrogen |

Sulphuric acid interacts feebly with aluminium, but nitric acid has no apparent effect. With a boiling solution of sodium or potassium hydroxide aluminium forms hydrogen and an aluminate, thus: —

| $6\,NaOH$ | + | $2\,Al$ | = | $2\,Na_3AlO_3$ | + | $3\,H_2$ |
|---|---|---|---|---|---|---|
| Sodium Hydroxide | | Aluminium | | Sodium Aluminate | | Hydrogen |

**Uses.** — The varied properties of aluminium adapt it to numerous uses. It is made into the metallic parts of military outfits, caps for jars, surgical instruments, cooking utensils, tubes, the fittings of boats, automobiles, and air ships, telephone receivers, scientific apparatus, parts of opera glasses and telescopes, the framework of cameras, stock patterns for foundry work, and hardware samples. Its attractive appearance has led to its extensive use as an ornamental metal, both in interior decorative work and in numerous small objects, such as trays, picture frames, hairpins, and combs. Aluminium leaf is used for decorating book covers and signs; a mixture of aluminium powder and an adhesive oil is likewise used as a paint for steam pipes, lamp-posts, radiators, smokestacks, and other metal objects exposed to heat or the weather. During the last few years aluminium wire has come into use as a conductor of electricity. Large quantities of aluminium powder are used to prepare metals whose oxides are reduced with difficulty and to produce high temperatures. For example, when a mixture of chromium oxide and powdered aluminium is ignited at one point by a special device the reduction thus initiated proceeds rapidly throughout the mixture and the intense heat thereby generated fuses the chromium, which can be removed from the crucible subsequently as a coherent mass; the aluminium oxide likewise melts and separates from the metal. The equation for the chemical change is —

$$\underset{\text{Chromium Oxide}}{Cr_2O_3} + \underset{\text{Aluminium}}{2\,Al} = \underset{\text{Chromium}}{2\,Cr} + \underset{\text{Aluminium Oxide}}{Al_2O_3}$$

Other metals hitherto rare or expensive can be similarly prepared. If a mixture of ferric oxide ($Fe_2O_3$) and powdered aluminium is ignited, molten steel at a temperature of about 3000° C. is produced. The apparatus in which the experiment is conducted is compact and portable and this method

is now utilized in welding iron rails, pipes, and rods, especially when the operation is more conveniently performed outside of a shop. These mixtures of aluminium and oxides are called "thermit," and the method is known as the Goldschmidt or aluminothermic method.

**Alloys.** — The alloy of aluminium and copper — aluminium bronze — has been described. (See Alloys of Copper.) **Magnalium** contains from 75 to 90 per cent of aluminium, the rest being magnesium; it is used in scientific instruments, *e.g.* as balance beams.

**Aluminium Oxide**, or **alumina**, $Al_2O_3$, is the only oxide of aluminium. Pure crystalline varieties of native alumina are known as **corundum**, while the impure forms are called **emery**; they are very hard substances, corundum being next below the diamond in the scale of hardness. Emery in the form of paper and wheels is used to grind and polish hard metals, plate glass, etc. The transparent colored kinds of corundum are prized as gems (see below).

Alumina is prepared as a white powder by heating the metal in the air or by heating the hydroxide. The product obtained by heating the hydroxide to a low temperature interacts with acids but the intensely heated oxide resembles the crystallized varieties in being almost insoluble in acids. The native oxide is converted into an aluminate and a sulphate respectively by fusing with a caustic alkali (*e.g.* potassium hydroxide) and with acid potassium sulphate ($HKSO_4$). Alumina melts in the oxyhydrogen flame, in the electric furnace, and during the reduction of oxides by aluminium (see Goldschmidt method above).

Compact crystalline alumina is manufactured from bauxite by an electrothermic process. It resembles native corundum and is used as an abrasive. This artificial alumina is known in trade as "alundum."

**Gems containing Aluminium.** — Corundum ($Al_2O_3$) has long been found in crystals in Ceylon, Siam, Burma, and other places in the Orient. The color is due to traces of impurities, usually oxides of metals. The sapphire is blue and the ruby is red. The Oriental topaz is yellow, the Oriental amethyst is purple, and the Oriental emerald is green. Montana furnishes many sapphires, the annual output being valued at about $90,000. These gems can be produced artificially by the Goldschmidt method. Spinels are complex compounds of aluminium. The typical or ruby spinel is magnesium aluminate ($MgAl_2O_4$). It resembles the true ruby in color. Other spinels differ from the ruby spinel both in color and in composition. Turquoise is a complex aluminium phosphate containing traces of copper. It has a beautiful robin's-egg-blue color, is compact, and may be worked into various shapes. Formerly turquoise came almost exclusively from Persia, but now New Mexico meets most demands. Topaz is a complex aluminium silicate containing fluorine, usually has a pale yellow color, and is found in many localities. Emerald is the most precious gem next to diamond and ruby. It is an aluminium silicate containing the rare element beryllium. The finest specimens have a deep emerald green color and come from Colombia, South America. Garnet is a complex silicate of aluminium and another metal, especially calcium, magnesium, iron, or manganese. The kind used as a gem has a deep red color and is rather abundant.

**Aluminium Hydroxide**, $Al(OH)_3$, is a white, jellylike solid formed by the interaction of an hydroxide and the solution of an aluminium salt, *e.g.*: —

| $AlCl_3$ | + | $3\,NH_4OH$ | = | $Al(OH)_3$ | + | $3\,NH_4Cl$ |
|---|---|---|---|---|---|---|
| Aluminium Chloride | | Ammonium Hydroxide | | Aluminium Hydroxide | | Ammonium Chloride |

It has weak acid and basic properties, the latter, however, being the stronger. Its acid property is shown by the formation of soluble saltlike compounds called aluminates upon the addition of an excess of sodium or potassium hydroxide, thus: —

| $Al(OH)_3$ | + | $3\,NaOH$ | = | $Na_3AlO_3$ | + | $3\,H_2O$ |
|---|---|---|---|---|---|---|
| Aluminium Hydroxide | | Sodium Hydroxide | | Sodium Aluminate | | Water |

The feeble basic property of aluminium hydroxide is illustrated by the fact that it does not form salts with such weak acids as carbonic, hydrosulphuric ($H_2S$), and sulphurous ($H_2SO_3$). Thus, when sodium carbonate or ammonium sulphide is added to the solution of an aluminium salt, aluminium hydroxide (not the carbonate or sulphide) is precipitated, *e.g.*: —

$$\underset{\text{Aluminium Chloride}}{2\,AlCl_3} + \underset{\text{Ammonium Sulphide}}{3\,(NH_4)_2S} + \underset{\text{Water}}{6\,H_2O} = \underset{\text{Aluminium Hydroxide}}{2\,Al(OH)_3} + \underset{\text{Ammonium Chloride}}{6\,NH_4Cl} + \underset{\text{Hydrogen Sulphide}}{3\,H_2S}$$

Like all bases, however, aluminium hydroxide interacts with strong acids and thereby forms salts, thus: —

$$\underset{\text{Aluminium Hydroxide}}{Al(OH)_3} + \underset{\text{Hydrochloric Acid}}{3\,HCl} = \underset{\text{Aluminium Chloride}}{AlCl_3} + \underset{\text{Water}}{3\,H_2O}$$

Commercial aluminium hydroxide is prepared by roasting bauxite or cryolite with sodium carbonate, extracting the resulting aluminate with water, and precipitating the hydroxide by passing carbon dioxide into the solution; the last operation may be represented by the equation: —

$$\underset{\text{Sodium Aluminate}}{2\,Na_3AlO_3} + \underset{\text{Carbon Dioxide}}{3\,CO_2} + \underset{\text{Water}}{3\,H_2O} = \underset{\text{Aluminium Hydroxide}}{2\,Al(OH)_3} + \underset{\text{Sodium Carbonate}}{3\,Na_2CO_3}$$

The aluminium hydroxide is dried and sold in the form of a white powder. There are several native aluminium hydroxides. **Bauxite** ($Al_2O_5H_4$ or $Al_2O_3 . 2\,H_2O$) contains ferric oxide ($Fe_2O_3$) as an impurity. It resembles clay in texture and color. The vast deposits found at Baux, in southern France, furnish much of the raw material for the manufacture of aluminium, though some is obtained from our Southern states. Hydrargyllite ($Al(OH)_3$) and diaspore ($AlO_2H$) are found in relatively small quantities.

**Aluminates** have been described in the foregoing paragraphs. They are compounds in which aluminium acts as an acid element, corresponding in this respect to the zincates. Aluminates are soluble to some extent in water and such solutions have an alkaline reaction owing to hydrolysis; the equation for the hydrolysis is —

$$Na_3AlO_3 + 3\ H_2O = Al(OH)_3 + 3\ NaOH$$

the alkaline reaction being caused by the hydroxyl ions liberated by the ionization of the sodium hydroxide. No aluminate is formed by adding an excess of ammonium hydroxide to aluminium hydroxide; this property is sometimes used to distinguish aluminium from zinc, since zinc hydroxide (a similar compound) forms a soluble complex compound by the interaction with ammonium hydroxide.

**Aluminium Sulphate**, $Al_2(SO_4)_3 . 18\ H_2O$, is a white, crystalline solid. The commercial salt has a variable composition; if pure, it dissolves readily and completely in water. It is extensively used as a mordant in dyeing (see below), as an ingredient of the size put upon paper to prevent the ink from spreading, and in preparing other aluminium compounds.

A solution of aluminium sulphate has an acid reaction on account of hydrolysis; the equation for the hydrolysis is —

$$Al_2(SO_4)_3 + 6\ H_2O = 2\ Al(OH)_3 + 3\ H_2SO_4$$

the acid reaction being due to the hydrogen ions liberated by the ionization of the sulphuric acid.

Aluminium sulphate is prepared from pure clay, bauxite, or cryolite. If clay or bauxite is heated with sulphuric acid and then allowed to cool, the product is impure aluminium sulphate, known as "alum cake," or if much iron is present, as "alumino-ferric cake"; it is used to purify sewage and for other purposes where iron and the other impurities are harmless. Purer aluminium sulphate is prepared by heating bauxite with sodium carbonate, extracting the sodium aluminate with water, and precipitating the aluminium as the hydrox-

ide with carbon dioxide gas; the relatively pure hydroxide is then changed into sulphate by treatment with sulphuric acid. The product, known as "concentrated alum," has the composition expressed by the formula $Al_2(SO_4)_3 . 20\,H_2O$, though separate crystals may contain only eighteen molecules of water of crystallization. By boiling cryolite with milk of lime, the sodium aluminate thereby formed may be changed into "concentrated alum," as described above. About 50,000 tons of "concentrated alum" are annually produced in the United States.

**Alum.** — When solutions of aluminium sulphate and potassium sulphate are mixed and concentrated by evaporation, transparent, colorless, glassy crystals are deposited. This solid is potassium alum or simply alum. It has the composition represented by the formula, $K_2Al_2(SO_4)_4 . 24\,H_2O$, or $K_2SO_4, Al_2(SO_4)_3 . 24\,H_2O$, and is sometimes called a double salt. It is the type of a class of similar salts called **alums**, which can be formed by mixing the solution of a sulphate of a trivalent metal (*e.g.* Al, Cr, Fe) with the solution of a sulphate of a univalent metal (*e.g.* K, Na, $NH_4$). Alums are rather soluble in water, and their solutions have an acid reaction owing to hydrolysis. (See Aluminium Sulphate.) They crystallize as octahedrons and contain twenty-four molecules of water of crystallization. When heated, alums lose their water of crystallization and some sulphur trioxide and fall to a white powder or porous mass known as **burnt alum**. Potassium alum is the most common, but ammonium and sodium alums are manufactured and used. Sodium alum is an ingredient of some baking powders. Burnt alum finds application as a medicine. Alum has been largely displaced by "concentrated alum," since aluminium sulphate has the same general properties; but the real alum is still used to some extent in dyeing and printing cloth, in tanning and paper making, in purifying water and sewage, as a medicine, for hardening plaster, in making wood and cloth fireproof, and in preparing other aluminium compounds.

Alum was known to the ancients, who used it in dyeing and tanning, and as a medicine. It was first manufactured in Europe, about the thirteenth century, from native alunite, which is an impure sulphate of aluminium, potassium, and iron. Alunite and alum slates or shales are now used to some extent, but most of the alum is made from bauxite.

Not all alums contain aluminium. As stated in the preceding paragraph, this metal may be replaced by iron, chromium, manganese, or any metal having the valence of three. Hence the general formula of an alum is $M_2(SO_4)_3 \cdot X_2SO_4 \cdot 24\,H_2O$, in which M may be aluminium, iron, chromium, etc., and X a metal (or group) like potassium, sodium, ammonium.

Alums are double salts, *i.e.* crystalline compounds of two or more normal salts. Their dilute aqueous solutions contain the ions of the separate salts and have properties which indicate the double nature, so to speak, of the salt in question. (Compare the Stassfurt salts.)

Alums and other aluminium salts are used as **mordants** in dyeing and calico printing. Some dyes must be fixed in the fabric by a metallic substance, otherwise the color could be easily removed. The cloth to be dyed or printed is impregnated or printed with a mordant, and then heated or treated with some substance to change the mordant into an insoluble compound. The mordanted cloth is next passed through a vat containing the solution of the dye, which unites chemically or mechanically (perhaps both) with the metallic compound, forming a colored compound. The latter is called a "lake"; it is relatively insoluble, and cannot be easily washed from the cloth, *i.e.* it is a fast color. Aluminium acetate or "red liquor," aluminium sulphate, and sodium aluminate, besides alum, are used as mordants for cotton, linen, and wool. The use of aluminium salts as mordants depends upon the fact that they hydrolyze readily; it is the resulting aluminium hydroxide, therefore, which is the effective metallic compound in dyeing.

**Cryolite** is a white, glassy, crystalline solid. It often resembles clouded ice, and its name means "ice stone."

Its composition corresponds to the formula $Na_3AlF_6$ (or $AlF_3 . 3\,NaF$). Small fragments melt easily, even in a candle flame, and color the Bunsen flame yellow. The only locality where it is found in commercial quantities is southern Greenland, which yields annually about 10,000 tons. It is used not only in manufacturing aluminium, but as a source of alum and aluminium hydroxide, pure sodium carbonate and hydroxide, hydrofluoric acid, and fluorides.

**Aluminium Chloride** when pure is a white powder, but it is often a yellowish, crystalline mass ($AlCl_3 . 6\,H_2O$). It is prepared by heating powdered aluminium in chlorine, or by passing chlorine over a heated mixture of aluminium oxide and carbon. Exposed to the air, it absorbs moisture and gives off fumes of hydrochloric acid. It dissolves in water with evolution of heat, and if the solution is heated, hydrochloric acid is expelled, owing to the hydrolysis of the chloride, thus: —

$$\underset{\text{Aluminium Chloride}}{AlCl_3} + \underset{\text{Water}}{3\,H_2O} = \underset{\text{Hydrochloric Acid}}{3\,HCl} + \underset{\text{Aluminium Hydroxide}}{Al(OH)_3}$$

This salt is used in organic chemistry.

**Tests for Aluminium.** — When a compound of aluminium is heated on charcoal with a blowpipe, cooled, moistened with cobaltous nitrate solution, and then reheated, the mass finally turns a beautiful blue color. Sodium hydroxide precipitates white gelatinous aluminium hydroxide, which dissolves in an excess of the alkali (NaOH), owing to the formation of soluble sodium aluminate. Aluminium hydroxide is insoluble in an excess of ammonium hydroxide (distinction from zinc hydroxide).

**Miscellaneous.** — It is evident from the preceding paragraphs that aluminium, like zinc, acts both as a metal and a

non-metal. Many soluble aluminium compounds yield colorless aluminium ions ($Al^{+++}$).

The atomic weight of this element is 27.1 and the valence is three.

**Clay** is a more or less impure aluminium silicate, formed by the slow decomposition of rocks containing aluminium, especially feldspar. Pure feldspar is a silicate of aluminium and sodium or potassium. The products of its decomposition are chiefly an insoluble aluminium silicate and a soluble alkaline silicate. The latter is washed away. The aluminium silicate which remains is pure clay or **kaolin**. The latter is really a hydrous silicate, having the composition corresponding to the formula $Al_2Si_2O_7 . 2\,H_2O$. The composition of clay varies, because it is seldom formed from pure feldspar. Pure kaolin is a white powdery substance, but most kaolin contains particles of mica and quartz. Ordinary clay contains many impurities, *e.g.* carbonates of calcium and magnesium, quartz, and iron compounds. All kinds of clay become plastic when wet and can be molded into various objects which shrink on drying but retain their general form; if heated, the dried clay does not melt (except at a very high temperature) but becomes a permanently hard mass. These properties (plasticity when wet and hardness when heated) make clay a most serviceable substance. For ages it has been made into useful and ornamental articles which may be roughly put into three comprehensive classes — porcelain, pottery, and materials of construction. The classes as well as the varieties in each class are the result of differences in quality and proportions of raw material and in method of heating. The subvarieties merge into each other.

**Porcelain** is the finest clay product. It is made by heating to a high temperature a mixture of very pure kaolin, fine sand, and a more fusible substance, usually feldspar, though sometimes chalk and gypsum are also used. The fused mass when cool is hard, dense, white, and translucent (if thin); it is often called "biscuit" or "biscuit ware." Although not very porous, its surface is glazed, partly for protection, partly for ornament. This is done by coating the ware with a thin mixture similar to that used for making the porcelain, but more easily fused, and then heating again so that the glaze will penetrate the clay. **Pottery** is a very large class and includes colored, white, glazed, and unglazed ware. The raw material is not as pure

as that used for porcelain, nor is the mixture heated to such a high temperature; the product, therefore, is rather coarse, opaque, heavy, and porous. The finer varieties, such as crockery, art pottery, and some kinds of stone ware, are glazed like porcelain. The coarser varieties, such as jugs and domestic utensils, are glazed by throwing salt into the oven just before the firing (*i.e.* the baking or heating) is over; the sodium in the sodium chloride forms a fusible aluminium silicate, which coats the surface. Unglazed pottery is familiar under different names, *e.g.* flower pots, tiles, terra cotta, and clay tobacco pipes. **Materials of construction** made from clay include some grades of stoneware, bricks, pipes, drain tile, etc. The raw material is usually impure and the firing is done at a low temperature. The product varies with the quality of the clay. Thus, ordinary clay containing iron compounds gives coarse red brick, while clay containing considerable silica gives bricks which withstand high temperature and are called fire-clay bricks. Pipe and drain tile, both glazed and porous, are used to convey water, sewage, and other fluids, and as a conduit for underground electric wires, especially wire cables.

### Problems and Exercises

1. What is the per cent of aluminium in (*a*) cryolite ($Na_3AlF_6$), (*b*) turquoise ($Al_2P_2O_8 \cdot H_6Al_2O_6 \cdot 2\,H_2O$), (*c*) corundum ($Al_2O_3$), (*d*) aluminium hydroxide?

2. What volume of oxygen at 15° C. and 760 mm. is needed to change 5 gm. of aluminium to aluminium oxide ($Al_2O_3$)?

3. If 6.917 gm. of aluminium bromide ($AlBr_3$) require 8.4429 gm. of silver to precipitate all the bromine, what is the atomic weight of aluminium? (Assume Ag = 107.88 and Br = 79.92.)

4. Write the formulas of the following compounds by applying the principle of valence and calculate the per cent of aluminium in each: Aluminium sulphide, aluminium phosphate, aluminium acetate, potassium aluminate.

# CHAPTER XXX

## Tin and Lead — Cerium and Thorium

Tin and lead are familiar metals. They have similar and useful properties, which give these metals and their compounds numerous applications.

### Tin

**Occurrence of Tin.** — Metallic tin is rarely if ever found. Tin dioxide (cassiterite or tin stone, $SnO_2$) is the only available ore. It is not widely distributed, but large deposits are found in England (at Cornwall), Germany (in Bohemia and Saxony), Australia, Tasmania, and the East Indian Islands, especially Banca and Billiton. A small quantity is found, but not mined, in the United States.

Tin is one of the oldest known metals. It is mentioned in the Pentateuch and was probably obtained long before the Christian era by the Phœnicians from the British Isles, which were called Cassiterides (from the Greek word *kassiteros*, meaning tin). Many ancient bronzes contain tin. The alchemists called it Jupiter, and used the metal and its compounds.

The Latin word *stannum* gives the symbol Sn and the terms *stannous* and *stannic*.

**Metallurgy of Tin.** — If the tin ore contains sulphur or arsenic, these impurities must be removed by roasting. The tin oxide is then reduced by heating it with coal in a reverberatory furnace; the simplest equation for this change is —

$$\underset{\text{Dioxide}}{SnO_2} + \underset{\text{Carbon}}{C} = \underset{\text{Tin}}{Sn} + \underset{\text{Dioxide}}{CO_2}$$

The molten tin, which collects at the bottom of the furnace, is drawn off and cast into bars or masses, which are often called block tin. Usually it is purified by melting it slowly on a hearth, inclined so that the more easily melted tin will flow down the hearth and leave the metallic impurities behind. This tin may be further purified by stirring the molten metal with a wooden pole or by holding billets of wood beneath its surface. The impurities, which are oxidized by the escaping gases, collect as a scum on the surface and are removed.

A small amount of tin is obtained by treating rejected tin plate or scrap tin with chlorine or some other active dissolving chemical.

**Properties of Tin.** — Tin is a white, lustrous metal. It is soft and malleable, and can be readily cut and hammered. It is softer than zinc but harder than lead. Its specific gravity is 7.3. Tin may be obtained in the crystalline form, and when a piece of such tin is bent it makes a crackling sound, which is caused by the friction of these crystals upon one another. It melts at about 233° C., and when heated to a higher temperature it burns, forming white tin oxide ($SnO_2$). The physical properties of tin, like those of zinc, vary with the temperature. One property of tin is rather striking. If kept at a low temperature for some time, ordinary tin changes slowly into a gray powder having a specific gravity of about 5.8. Experiment shows that this transformation begins at 20° C., and this temperature is called the transition point. A similar phenomenon is exhibited by sulphur. (See Chapter XVIII, Different Forms of Sulphur.) Sometimes this "tin disease," as it might be called, attacks the pipes of church organs. The appearance of a sheet of tin affected by "tin disease" is shown in Figure 78. Concentrated hydrochloric acid

changes tin into stannous chloride ($SnCl_2$), hot concentrated sulphuric acid converts it into stannous sulphate ($SnSO_4$), while commercial nitric acid transforms it into a white solid known as metastannic acid. With sodium hydroxide

FIG. 78. — Sheet of tin affected by "tin disease" (enlarged one and one half times).

tin forms sodium metastannate ($Na_2SnO_3$). Zinc precipitates tin from its solutions as a grayish black, spongy mass, which is sometimes filled with bright scales. This is due to the fact that zinc precedes tin (by several places) in the electromotive series of the metals. (See Chapter XXVI, Electromotive Series of Metals.)

**Uses of Tin.** — Tin is so permanent in air, water, weak acids (like vinegar and fruit acids), and alkalies that it is extensively used in making scientific apparatus and as a protective coating for metals. Condensing pipes in stills are often made of tin. Ordinary tinware is sheet iron coated with tin. The tin plate (sheet tin, or simply "tin") is made by dipping very clean sheet iron into molten tin. Tacks, nails, and many small iron objects are similarly tinned. Copper coated with tin is made into vessels for cooking, and brass coated with tin is made into pins. Large

quantities of tin plate are used to cover roofs. Tinned iron does not rust until the tin is worn off and the iron exposed, and then the rusting proceeds rapidly. Tin is also hammered into thin sheets called tin foil, though much tin foil contains lead. Many useful alloys contain tin as an essential ingredient.

**Alloys of Tin** containing a minor percentage of tin are bronze, gun metal, speculum metal, type metal, anti-friction metals, and fusible alloys. **Britannia metal** contains about 90 per cent tin, 8 per cent antimony, and the rest mainly copper. It is a white metal, and was formerly made into tableware. **White metal** contains less tin and more antimony than Britannia, though the composition varies. It resembles Britannia. The harder varieties of white metal are used as parts of machinery, and the softer kinds are made into ornaments and cheap jewelry. **Pewter** and **solder** contain varying proportions of tin and lead. Plumbers' solder, or soft solder, is about one third tin and two thirds lead; it is harder than either constituent, but melts at a lower temperature. Tin amalgam is sometimes used to coat mirrors.

**Compounds of Tin.** — Tin forms two series of compounds, the stannous and the stannic. The valence of tin is two in the stannous compounds and four in the stannic. **Stannic oxide** ($SnO_2$) has already been mentioned as the chief ore of tin and the product formed when tin is burned. The artificial oxide is faint yellow when hot and white when cold. The native oxide is a brown or black, lustrous, (often) crystalline solid. Irregular pebbles called stream tin occur in some localities near rivers. **Stannous chloride** ($SnCl_2$) is formed by the interaction of hydrochloric acid and tin. From the concentrated solution a greenish salt crystallizes ($SnCl_2.2\,H_2O$), known as the tin crystals or salt of tin.

Stannous chloride passes readily into stannic chloride ($SnCl_4$) when added to mercuric chloride solution. The simplest equation for this change is —

| $SnCl_2$ | + | $2\,HgCl_2$ | = | $SnCl_4$ | + | $2\,HgCl$ |
|---|---|---|---|---|---|---|
| Stannous Chloride | | Mercuric Chloride | | Stannic Chloride | | Mercurous Chloride |

By an extension of the simplest idea of oxidation and reduction, the stannous chloride in this change is said to be oxidized to stannic chloride and the mercuric chloride to be reduced to mercurous chloride. An excess of stannous chloride reduces the white mercurous chloride to a gray precipitate of finely divided mercury; this reaction is used as a **test for tin.** (Compare tests for Mercury, Chapter XXVIII.) Stannous chloride is often used as a reducing agent and as a mordant in calico dyeing and printing. **Stannic chloride** ($SnCl_4$) is a colorless, fuming liquid; it forms a crystalline hydrate ($SnCl_4 . 5\,H_2O$), known commercially as **oxymuriate of tin**, which is used as a mordant. **Ammonium stannic chloride** ($(NH_4)_2SnCl_6$), or "pink salt," is also used as a mordant. Tin mordants produce brilliant colors. **Sodium stannate** ($Na_2SnO_3 . 3\,H_2O$) is extensively used to prepare cotton cloth for printing. With hydrogen sulphide, stannous compounds form brown **stannous sulphide** ($SnS$), and stannic compounds form yellow **stannic sulphide** ($SnS_2$); both sulphides dissolve in yellow ammonium sulphide, owing to the formation of soluble sulpho-salts of tin.

**Miscellaneous.** — Tin, like zinc and aluminium, acts both as a metal and a non-metal. Thus, there are the stannous and stannic salts and the stannates. Solutions of stannous salts contain stannous ions ($Sn^{++}$).

The atomic weight of tin is 119.0, and the valence, as stated above, is two in stannous and four in stannic compounds.

## Lead

**Occurrence of Lead.** — Metallic lead is occasionally found in small quantities. The most abundant ore is lead sulphide (galena, PbS). Other native compounds, doubtless formed by the alteration of galena, are the carbonate (cerussite, $PbCO_3$), the sulphate (anglesite, $PbSO_4$), and the phosphate (pyromorphite, $Pb_5Cl(PO_4)_3$). Lead compounds are widely distributed, but the source of commercial lead is the sulphide.

Lead has been used by civilized people since the dawn of history. The Chinese have used it for ages to line chests in which tea is stored and transported. The Romans, who obtained it from Spain, called it *plumbum nigrum, i.e.* black lead. The symbol Pb comes from *plumbum*. The ancients also used lead compounds (especially the carbonate and red oxide) as paints and cosmetics.

Lead ores come from the United States, Spain, Germany, Mexico, New South Wales, and England. In the United States the ores are found mainly in the Middle West (Illinois, Iowa, Wisconsin, and Missouri), Colorado, Idaho, and Utah.

**Metallurgy of Lead.** — Lead is obtained almost exclusively from galena. (1) In the reduction process the ore is roasted in a reverberatory furnace until a part of the sulphide is changed into lead oxide and lead sulphate. The equations for these changes are —

$$\underset{\substack{\text{Lead}\\\text{Sulphide}}}{2\,PbS} + \underset{\text{Oxygen}}{3\,O_2} = \underset{\substack{\text{Lead}\\\text{Oxide}}}{2\,PbO} + \underset{\substack{\text{Sulphur}\\\text{Dioxide}}}{2\,SO_2}$$

$$\underset{\substack{\text{Lead}\\\text{Sulphide}}}{PbS} + \underset{\text{Oxygen}}{2\,O_2} = \underset{\substack{\text{Lead}\\\text{Sulphate}}}{PbSO_4}$$

The air is then shut off and the mixture of the three lead compounds is heated to a higher temperature. By this operation the lead sulphide interacts with the other lead compounds, forming lead and sulphur dioxide, thus : —

$$\underset{\text{Lead Sulphide}}{2\,PbS} + \underset{\text{Lead Sulphate}}{PbSO_4} + \underset{\text{Lead Oxide}}{2\,PbO} = \underset{\text{Lead}}{5\,Pb} + \underset{\text{Sulphur Dioxide}}{3\,SO_2}$$

(2) Ores poor in lead are sometimes reduced by roasting with iron, which combines with the sulphur, leaving the lead free, thus : —

$$\underset{\text{Lead Sulphide}}{PbS} + \underset{\text{Iron}}{Fe} = \underset{\text{Lead}}{Pb} + \underset{\text{Iron Sulphide}}{FeS}$$

**Properties of Lead.** — Lead is a blue-gray metal. When scraped or cut, it has a brilliant luster, which soon disappears, owing to the formation of a film of oxide or other lead compound. This coating protects the lead from further change. It is a soft metal, and can be scratched with the finger nail. It discolors the hands, and when drawn across a rough surface it leaves a black mark. For this reason it is sometimes erroneously called black lead. (See Graphite.) Lead is not tough enough to be hammered into foil or drawn into fine wire, but it can be pressed into pipe and rolled into sheets. It is a heavy metal, its specific gravity being about 11.4; with the exception of mercury, it is the heaviest of the familiar metals. It melts at 327° C., or about 100° higher than tin and 100° lower than zinc. Lead, when heated to a low temperature in the air, changes into the monoxide (PbO); at higher temperatures (about 350° C. and above) the tetroxide ($Pb_3O_4$) is formed. Hydrochloric and sulphuric acids exert only a slight chemical action upon compact lead. (See Lead Sulphate.) Nitric acid changes it into lead nitrate ($Pb(NO_3)_2$). Acetic acid (or vinegar) and acids from fruits and vegetables change it into soluble, poisonous compounds; hence cheap tin-plated vessels, which sometimes contain lead, should never be used in cooking. Zinc and iron precipitate lead from its solutions as a grayish mass, which often has a beautiful treelike appearance.

This displacement, as in the case of tin, is due to the fact that lead is lower than zinc and iron in the electromotive series.

**Lead in Drinking Water.** — Lead is slowly changed into soluble compounds by water containing free oxygen, carbon dioxide, ammonia, nitrates, or chlorides. But water containing sulphates or carbonates forms an insoluble coating on the lead, thus protecting it from further action. All lead salts are poisonous; and if taken into the system they slowly accumulate and ultimately cause serious and dangerous illness. Water suspected of attacking lead should never be drunk after it has been standing very long in lead pipes, but should be allowed to flow until the pipe has been filled with fresh water. It is sometimes safer to substitute an iron or block tin pipe for the customary lead service pipe.

**Uses of Lead.** — Lead on account of its plasticity when warm is extensively made into pipe, which can be easily cut, bent, and united (by solder). Lead pipe is not only used to convey water to and from parts of buildings, but as a sheath for electric wires, both overhead and underground. In the form of sheets it is used to cover roofs and to line sinks, cisterns, and the cells employed in some electrolytic processes. The lead chambers and evaporating pans used in manufacturing sulphuric acid are made of sheet lead. Shot and bullets are lead (alloyed with a little arsenic).

**The Alloys of Lead** are important. **Type metal** contains 70 to 80 per cent lead; the other constituents are tin and antimony. The alloy is harder than the lead itself and expands on cooling, thereby making the face of the type sharp and hard. **Solder**, **pewter**, and **fusible alloys** contain lead as an essential constituent. (See these Alloys.)

**Lead Oxides.** — There are three important oxides. **Lead monoxide** (PbO) is a yellowish powder known as **massicot**, or a buff-colored crystalline mass called **litharge.** It is formed by heating lead above its melting point in a current of air. It is made this way, though considerable is obtained as a by-product in separating silver from lead. (See Cupellation.) Large quantities are used in preparing certain oils and varnishes, flint glass, other lead compounds, and as a glaze for pottery. **Lead tetroxide** (red lead or minium, $Pb_3O_4$) is a red powder, varying somewhat in color and composition. It is prepared by heating lead (or lead monoxide) to about 350° C. It is used in making flint glass. Pure grades are made into artists' paint, but the cheap variety is used to paint structural iron work (bridges, gasometers, etc.), hulls of vessels, and agricultural implements. A mixture of red lead and oil is used in plumbing and gas fitting to make joints tight. **Orange mineral** has the same composition as red lead, although its color is lighter; its uses are the same. **Lead dioxide** (lead peroxide, $PbO_2$) is a brown powder formed by treating lead tetroxide with nitric acid. It is used in storage batteries and as an oxidizing agent.

**Lead Carbonate,** $PbCO_3$, is found native as the transparent, crystalline mineral cerussite. It is obtained as a white powder by adding ammonium carbonate solution to lead nitrate solution. Sodium or potassium carbonate, however, forms basic lead carbonates, whose composition depends upon the temperature. The most important of these basic carbonates usually has the composition corresponding to the formula $2\,PbCO_3 . Pb(OH)_2$, and is known as **white lead.** It is a heavy white powder which mixes well with linseed oil, and is used extensively as a white paint and as the basis of many colored paints. Its value as a

paint is largely due to its superior covering power, *i.e.* a very thin layer produces a perfectly white, opaque surface. It is sometimes adulterated with zinc oxide or barium sulphate, — cheaper white solids that have less covering power. One objection to white lead paint is the darkening due to the formation of lead sulphide by the interaction with hydrogen sulphide. (See Sulphides.)

White lead is manufactured by several processes. The **Dutch process** is the oldest, having been used as early as 1622. It is essentially the same to-day, though many details have been improved. Perforated disks of lead are put in earthenware pots which have a separate compartment at the bottom containing a weak solution of acetic acid (about as strong as vinegar). These pots are arranged in tiers in a large building, and spent tan bark is placed between each tier. The building is now closed, except openings for the entrance and exit of air and steam. The heat volatilizes the acetic acid, which changes the lead into a lead acetate. The tan bark ferments and liberates carbon dioxide, which changes the lead acetate into basic lead carbonate. The whole operation requires from sixty to one hundred days. Other processes, much the same as the Dutch process, are used, their chief aim being to lessen the time of manufacture.

**Lead Sulphide**, PbS. — Native lead sulphide is the mineral galena, the chief ore of lead. It resembles lead in appearance, but is harder and is usually crystallized as cubes, octahedrons, or their combinations. It has a perfect cubic cleavage, *i.e.* it breaks into cubes or fragments more or less rectangular. It is easily changed into lead by heating it alone or with sodium carbonate on charcoal. Lead sulphide as prepared in the laboratory is a black solid. Black lead sulphide is readily precipitated from a lead salt solution by hydrogen sulphide. Its formation is a **test for lead.** It is changed into lead chloride by concentrated hydrochloric acid and into lead sulphate by concentrated nitric acid. Additional tests for lead are the formation of the sulphate and chromate, as described in the next paragraph.

**Other Compounds of Lead**, which are important, are the chloride, sulphate, nitrate, chromate, and acetate. **Lead chloride** ($PbCl_2$) is a white solid formed by adding hydrochloric acid or a soluble chloride to a cold solution of a lead salt. It dissolves in hot water. **Lead sulphate** ($PbSO_4$) is a white solid formed by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is very slightly soluble in water, but soluble in sulphuric acid, hence crude sulphuric acid often contains lead sulphate. **Lead nitrate** ($Pb(NO_3)_2$) is a white crystalline solid formed by dissolving lead (or better, lead monoxide) in nitric acid. When heated, it decomposes into lead oxide (PbO), nitrogen peroxide, and oxygen. **Lead chromate** ($PbCrO_4$) is a yellow solid formed by adding a solution of a lead compound to a solution of potassium chromate or potassium dichromate. It is sometimes called "chrome yellow." **Lead acetate** ($Pb(C_2H_3O_2)_2$) is a white crystalline solid formed by the action of acetic acid upon lead or lead oxide (PbO). It is very soluble in water and is often called "sugar of lead."

**Miscellaneous.** — Aqueous solutions of lead compounds may contain several kinds of ions. The common compounds, such as lead chloride, lead nitrate, and lead acetate, yield a colorless ion ($Pb^{++}$). Other compounds yield ions containing oxygen as well as complex ions. Compounds in which lead acts as a non-metal are known, *e.g.* **sodium plumbate** ($Na_2PbO_3$).

The atomic weight of lead is 207.10. The valence is two in many of its compounds; it is four in lead dioxide ($PbO_2$) and plumbates.

## Cerium and Thorium

**Cerium** (Ce) and **Thorium** (Th) are members of a family of rare elements in the same periodic group as tin and lead. They are constituents of rare minerals, but their compounds

are prepared from a complex mineral substance named monazite sand. The oxides of thorium and cerium are the essential compounds in the Welsbach mantles. In making the mantles, the cotton bag is dipped into a solution of thorium and cerium nitrates, and then burned. The cotton is destroyed by heat and the nitrates are converted into a firm mass of oxides, which retain the shape of the mantle. The proportion is about 1 per cent cerium oxide ($CeO_2$) and 99 per cent thorium oxide ($ThO_2$), this being the proper mixture for a brilliant flame of suitable color. (See also Bunsen Flame, Chapter XVI.)

Thorium compounds are radio-active. (See Radio-activity.)

### Problems and Exercises

1. What is the per cent of lead in (*a*) galena (PbS), (*b*) cerussite ($PbCO_3$), (*c*) anglesite ($PbSO_4$), (*d*) crystallized lead acetate ($Pb(C_2H_3O_2)_2 . 3\ H_2O$)?

2. How much litharge may be made from 40.5 gm. of lead? (Assume Pb + O = PbO.)

3. What is the per cent of tin in (*a*) tinstone ($SnO_2$), (*b*) stannous chloride ($SnCl_2$), (*c*) stannic chloride ($SnCl_4$)?

4. If 100 gm. of tin form 127.1 gm. of stannic oxide ($SnO_2$), what is the atomic weight of tin?

5. By analysis 100 gm. of lead monoxide yielded 7.1724 gm. of oxygen. What is the atomic weight of lead?

6. Suppose 5 gm. of lead chloride yield 5.16 gm. of silver chloride, what is the atomic weight of lead?

7. Calculate the percentage composition of stannous oxide and stannic oxide, and illustrate the law of multiple proportions by the values thus obtained.

8. Write the formulas of the following compounds by applying the principle of valence: Lead iodide, stannous bromide, thorium nitrate, cerium sulphate.

9. A rectangular block of tin measures 30 × 10 × 5 cm., and weighs 10,950 gm. What is its specific gravity?

10. A cubic foot of lead weighs 710 pounds. What is the weight in grams of 1 cc.?

# CHAPTER XXXI

## Manganese

**Occurrence.** — This metal is not found free in nature, but its oxides are widely distributed and rather abundant. The chief compound is manganese dioxide (pyrolusite, $MnO_2$). Other native compounds of manganese are braunite ($Mn_2O_3$), hausmannite ($Mn_3O_4$), manganite ($MnO(OH)$ or $MnO_2H$), and rhodocroisite ($MnCO_3$).

**Preparation, Properties, and Uses.** — Manganese is prepared by heating manganese dioxide with charcoal in an electric furnace, but the purest quality is made by the aluminothermic method.

The equation for the latter change is —

$$\underset{\text{Aluminium}}{4\,Al} + \underset{\substack{\text{Manganese}\\\text{Dioxide}}}{3\,MnO_2} = \underset{\text{Manganese}}{3\,Mn} + \underset{\substack{\text{Aluminium}\\\text{Oxide}}}{2\,Al_2O_3}$$

The metal is gray-red, hard, and brittle. If pure, it is permanent in the air. It interacts with dilute acids. Its chief property is the ready formation of alloys, especially with iron, copper, zinc, and nickel.

**Alloys of Manganese** and iron are extensively used in the manufacture of Bessemer steel. (See Steel.) **Spiegel iron** contains from 5 to 20 per cent of manganese, while **ferromanganese** contains 20 per cent or more. Other alloys are finding applications, now that pure manganese is available.

**Manganese Dioxide,** $MnO_2$, is the most abundant and important compound. It is a black solid and is often called

black oxide of manganese. When heated to a high temperature, it yields oxygen; and when heated with hydrochloric acid, the two compounds interact, forming manganous chloride, chlorine, and water, thus: —

$$\underset{\text{Manganese Dioxide}}{MnO_2} + \underset{\text{Hydrochloric Acid}}{4\,HCl} = \underset{\text{Manganous Chloride}}{MnCl_2} + \underset{\text{Chlorine}}{Cl_2} + \underset{\text{Water}}{2\,H_2O}$$

It colors glass and borax a beautiful amethyst, and is often used in glass making to neutralize the green color that would be caused by iron compounds in the sand. Large quantities are used in the manufacture of oxygen, chlorine, glass, and manganese alloys and compounds.

A borax bead is colored amethyst by manganese compounds in the oxidizing flame but is colorless in the reducing flame — a **test for manganese.**

The manganese dioxide used in the manufacture of chlorine is recovered by the **Weldon process.** The impure manganous chloride solution from the chlorine still is treated with calcium carbonate to neutralize the free acid and precipitate any iron present. Lime is added to the clear solution of manganous chloride, and air is blown into the mixture. The manganous chloride is changed into manganous hydroxide ($Mn(OH)_2$), which interacts with the oxygen (of the air) and lime, forming chiefly calcium manganite ($CaMnO_3$). After this mixture has settled, the calcium chloride is drawn off, and the manganese compound, which is called "Weldon mud," is used to generate more chlorine.

Manganese dioxide was used by the ancients to decolorize glass, but its nature was misunderstood. They confused it with an iron oxide called magnesia stone, and the alchemists in the Middle Ages gave the name magnesia to this manganese dioxide. Later they called it *magnesia nigra*, or black magnesia, to distinguish it from *magnesia alba*, or white magnesia (MgO), supposing the two were related. Manganese was isolated in 1774, and later was given the specific name manganesium, which was soon shortened to manganese.

**Potassium Permanganate**, $KMnO_4$, is a dark purple, glistening, crystalline solid, though the crystals sometimes

appear black, with greenish luster. It is very soluble in water, and solution is red, purple, or black, according to the concentration. Potassium permanganate gives up its oxygen readily and is frequently used as an oxidizing agent in the laboratory. It is also used as a disinfectant, a medicine, in bleaching and dyeing, in coloring wood brown, and in purifying gases, such as hydrogen, ammonia, and carbon dioxide.

Potassium permanganate is manufactured by oxidizing a mixture of manganese dioxide and potassium hydroxide, and treating the resulting potassium manganate with sulphuric acid, carbon dioxide, or chlorine. The essential reactions are represented thus: —

$$\underset{\text{Manganese Dioxide}}{MnO_2} + 2\,\underset{\text{Potassium Hydroxide}}{KOH} + O = \underset{\text{Potassium Manganate}}{K_2MnO_4} + H_2O$$

$$3\,K_2MnO_4 + 2\,CO_2 = 2\,\underset{\text{Potassium Permanganate}}{KMnO_4} + 2\,K_2CO_3 + MnO_2$$

The uses of potassium permanganate depend mainly upon its oxidizing power, that is, upon the property of liberating nascent oxygen readily. In an acid solution the action is represented thus: —

$$\underset{\text{Potassium Permanganate}}{2\,KMnO_4} + \underset{\text{Sulphuric Acid}}{3\,H_2SO_4} = \underset{\text{Oxygen}}{5\,O} + \underset{\text{Manganese Sulphate}}{2\,MnSO_4} + \underset{\text{Potassium Sulphate}}{K_2SO_4} + \underset{\text{Water}}{3\,H_2O}$$

In neutral or alkaline solutions the action is as follows: —

$$2\,KMnO_4 + 5\,H_2O = 3\,O + 2\,Mn(OH)_4 + 2\,KOH$$

The liberated oxygen oxidizes organic matter or any other oxidizable substance, and the solution becomes brown or colorless, owing to the reduction of the potassium permanganate and the transformation into manganese compounds having a faint color or none.

**Compounds of Manganese** are numerous, often complex, and closely related. There are four oxides besides manganese dioxide. Three **manganous compounds** are important, the chloride ($MnCl_2$), the sulphate ($MnSO_4$), and the sulphide (MnS); in these and other manganous compounds the manganese plays the rôle of a metal. The chloride and sulphate are pink, crystalline salts. The sulphide is obtained as a flesh-colored precipitate by adding ammonium sulphide to the solution of a manganous salt, the color distinguishing it from all other sulphides; its formation is often used as a **test for manganese.** **Manganates** are salts of the hypothetical manganic acid ($H_2MnO_4$); the manganese in them acts as a non-metal. Potassium manganate ($K_2MnO_4$) is obtained as a green mass by fusing a mixture of a manganese compound, potassium hydroxide (or carbonate), and potassium nitrate. Its formation on a small scale constitutes a **test for manganese.** One equation for this chemical change is given on the preceding page; another is as follows:

| $MnO_2$ | + | $K_2CO_3$ | + | O | = | $K_2MnO_4$ | + | $CO_2$ |
|---|---|---|---|---|---|---|---|---|
| Manganese Dioxide | | Potassium Carbonate | | | | Potassium Manganate | | Carbon Dioxide |

Sodium manganate ($Na_2MnO_4$) is used in solution as a disinfectant, but sodium permanganate ($NaMnO_4$) is more effective and is sold in solution as "Condy's liquid."

**Miscellaneous.** — Manganese has a variable valence. It is two in manganous compounds (*e.g.* MnO, $Mn(OH)_2$, MnS, and $MnSO_4$), three in manganic compounds (*e.g.* $Mn_2O_3$), four in manganese dioxide ($MnO_2$) and in manganites, six in manganates (*e.g.* $K_2MnO_4$), and seven in permanganates (*e.g.* $KMnO_4$). The valence of the radical $MnO_4$ is two in manganates and one in permanganates.

Manganese compounds yield several kinds of ions, *e.g.* the

delicate pink manganese ion ($Mn^{++}$), and the purple permanganate ion ($MnO_4^-$).

The atomic weight of manganese is 54.93. Manganese apparently occupies an isolated position in Group VII of the periodic classification.

## Problems and Exercises

1. What is the per cent of manganese in (*a*) manganese dioxide ($MnO_2$), (*b*) manganese sulphide (MnS), (*c*) manganese alum ($K_2Mn_2(SO_4)_4 . 24\ H_2O$)?

2. How much manganese ore containing 85 per cent of manganese dioxide is needed to prepare 300 lb. of chlorine? (Assume $MnO_2 + 4\ HCl = Cl_2 + MnCl_2 + 2\ H_2O$.)

3. Suppose 10.6647 gm. of manganous oxide (MnO) yield 22.6875 gm. of manganese sulphate ($MnSO_4$). What is the atomic weight of manganese, on the assumption that 16 and 32.07 are the atomic weights of oxygen and sulphur respectively?

4. Write the formulas of the following compounds by applying the principle of valence, and calculate the per cent of manganese in each: Calcium permanganate, manganese heptoxide, permanganic acid, calcium manganate.

## CHAPTER XXXII

### Chromium — Uranium — Radio-Activity

**Occurrence.** — Metallic chromium is never found free. Its chief ore is ferrous chromite, or chrome iron ore, $FeCr_2O_4$. Native lead chromate (crocoite, or crocoisite, $PbCrO_4$) is less common. Traces of chromium occur in many green minerals and rocks, *e.g.* emerald, serpentine, and verde antique marble.

The name chromium comes from the Greek *chroma*, meaning color, and emphasizes the fact that most chromium compounds have conspicuous colors.

**Preparation, Properties, and Uses.** — Chromium was a rare metal until Moissan prepared it, in 1894, by heating a mixture of chromite and carbon in an electric furnace. The product contained carbon and was refined by fusing it with lime. Pure chromium is now prepared by the aluminothermic method. (See Thermit.)

Chromium is a lustrous gray metal. It takes a good polish, which is not removed by exposure to air. It is hard and brittle, and can be polished without difficulty. Its specific gravity is about 6.9. It is not attracted by a magnet. It can be fused only in the electric furnace or in the aluminothermic crucible.

Chromium is used to harden the steel that is made into armor plates, hard tools, projectiles, safes and vaults, and certain parts of machines used to crush gold-bearing quartz. This hardened steel is called chromium steel. The commercial form of chromium is usually an alloy of 65 to 80

per cent chromium, a little carbon, and the rest iron; this alloy is called ferrochrome.

**Compounds of Chromium** are numerous, some are complex, many pass readily into one another, and a few have industrial applications. The most important are potassium chromate, potassium dichromate, chrome alum, and lead chromate.

**Potassium Chromate, $K_2CrO_4$, and Potassium Dichromate, or Bichromate, $K_2Cr_2O_7$.** — These compounds are manufactured from chrome iron ore. The crushed ore is mixed with lime and potassium carbonate and roasted in a reverberatory furnace; air is freely admitted and the mass frequently raked. By this operation the ore is oxidized into a mixture of calcium and potassium chromates. The mass is cooled, pulverized, and treated with a hot solution of potassium sulphate, which changes the calcium chromate into potassium chromate, thus : —

$$\underset{\text{Calcium Chromate}}{CaCrO_4} + \underset{\text{Potassium Sulphate}}{K_2SO_4} = \underset{\text{Potassium Chromate}}{K_2CrO_4} + \underset{\text{Calcium Sulphate}}{CaSO_4}$$

The solution of potassium chromate is filtered, concentrated, and changed by sulphuric acid into potassium dichromate; the latter is purified by recrystallization from water. **Potassium chromate** is a lemon-yellow, crystalline solid, which contains no water of crystallization. It is very soluble in water and gives a yellow solution. Acids change it into the dichromate, thus : —

$$\underset{\text{Potassium Chromate}}{2\,K_2CrO_4} + \underset{\text{Sulphuric Acid}}{H_2SO_4} = \underset{\text{Potassium Dichromate}}{K_2Cr_2O_7} + \underset{\text{Potassium Sulphate}}{K_2SO_4} + \underset{\text{Water}}{H_2O}$$

Potassium chromate is also formed as a yellow mass by fusing intensely on porcelain (or platinum) a mixture of a

chromium compound, potassium carbonate, and potassium nitrate. When the mass is boiled with an excess of acetic acid to decompose the carbonate and expel the carbon dioxide, and then added to a lead salt solution, yellow lead chromate is precipitated. This experiment is often used as a **test for chromium.** (See also Lead Chromate.) **Potassium dichromate** is a red solid, which is prepared as described above. It is less soluble in water than potassium chromate, and yields a pale yellow or red solution according to the concentration. Hydroxides change it into the chromate, thus: —

$$\underset{\text{Potassium Dichromate}}{K_2Cr_2O_7} + \underset{\text{Potassium Hydroxide}}{2\,KOH} = \underset{\text{Potassium Chromate}}{2\,K_2CrO_4} + \underset{\text{Water}}{H_2O}$$

Potassium dichromate is used in dyeing, calico printing, and tanning, in bleaching oils, and in manufacturing chromium compounds and dyestuffs. Its uses depend mainly upon the fact that it is an oxidizing agent. When potassium dichromate and sulphuric acid are mixed, the equation for the reaction may be written: —

$$\underset{\text{Potassium Dichromate}}{K_2Cr_2O_7} + \underset{\text{Sulphuric Acid}}{4\,H_2SO_4} = \underset{\text{Oxygen}}{3\,O} + \underset{\text{Potassium Sulphate}}{K_2SO_4} + \underset{\text{Chromium Sulphate}}{Cr_2(SO_4)_3} + 4\,H_2O$$

Some oxidizable substance, however, such as ferrous sulphate, must be present to use up the liberated oxygen, thus: —

$$\underset{\text{Ferrous Sulphate}}{6\,FeSO_4} + 3\,H_2SO_4 + 3\,O = \underset{\text{Ferric Sulphate}}{3\,Fe_2(SO_4)_3} + 3\,H_2O$$

The complete chemical change is often expressed as follows: —

$$K_2Cr_2O_7 + 7\,H_2SO_4 + 6\,FeSO_4 = 3\,Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O$$

Potassium chromate and dichromate are being replaced somewhat by the corresponding sodium salts, because the latter are cheaper, more soluble, and have analogous properties. The potassium salts are anhydrous, but crystallized sodium chromate is $Na_2CrO_4 . 10\ H_2O$ and crystallized sodium dichromate is $Na_2Cr_2O_7 \cdot 2\ H_2O$.

**Chrome Alum**, $K_2Cr_2(SO_4)_4 . 24\ H_2O$, is a purple, crystalline solid. It is analogous in composition and similar in properties to ordinary alum, but it contains chromium instead of aluminium. It can be prepared by mixing potassium and chromium sulphates in the proper proportion, or by passing sulphur dioxide into a solution of potassium dichromate containing sulphuric acid. The commercial substance is a by-product obtained in the manufacture of the dyestuff alizarin. Chrome alum is used as a mordant in dyeing and calico printing and in tanning.

**Lead Chromate**, $PbCrO_4$, is a bright yellow solid, formed by adding potassium chromate or dichromate to a solution of a lead salt. An equation for the chemical change is —

$$\underset{\text{Potassium Dichromate}}{K_2Cr_2O_7} + 2\ \underset{\text{Lead Nitrate}}{Pb(NO_3)_2} + \underset{\text{Water}}{H_2O} = 2\ \underset{\text{Lead Chromate}}{PbCrO_4} + 2\ \underset{\text{Potassium Nitrate}}{KNO_3} + 2\ \underset{\text{Nitric Acid}}{HNO_3}$$

It is known as **chrome yellow**, and is used in making yellow paint. When boiled with sodium hydroxide, lead chromate is changed into a basic chromate ($PbCrO_4 . PbO . H_2O$) called chrome red or chrome orange, depending on the color.

The precipitation of lead chromate by the interaction of a dissolved lead salt and a dissolved chromate (or dichromate) is often used as a **test for chromium.**

**Chromium forms Four Series of Compounds**, the chromous, the chromic, the chromites, and the chromates (mono- and di-). In the chromous and chromic compounds, chromium acts as a metal, but in chromites and chromates it acts as a non-metal.

**Chromous Compounds** may be regarded as derived from chromous oxide (CrO). As a class they are so easily oxidized into chromic compounds that they are difficult to prepare and keep.

**Chromic Compounds** may be regarded as derivatives of chromic oxide ($Cr_2O_3$). This is a bright green powder prepared by heating chromic hydroxide ($Cr(OH)_3$), and is the basis of the chrome green pigments used to color glass and ornament porcelain. When chromium compounds are heated with borax, they color the bead green in both flames, owing to the formation of this oxide ($Cr_2O_3$). If potassium dichromate and boric acid are mixed and heated, and then treated with water, a hydrated chromic oxide is formed called Guignet's green ($Cr_2O_3 . 2\ H_2O$); it gives a permanent color and is extensively used. There are several chromic hydroxides. The typical one has the composition represented by the formula $Cr(OH)_3$. It is a bluish solid formed by the interaction of a chromic compound (*e.g.* chrome alum) and an alkaline hydroxide or sulphide. The precipitation of chromic hydroxide by ammonium sulphide is due to the fact that chromic sulphide (which we might expect to be formed) hydrolyzes, yielding chromic hydroxide and hydrogen sulphide. (Compare Aluminium Hydroxide, Chapter XXIX.)

Chromic hydroxide is soluble in an excess of sodium (or potassium) hydroxide. That is, it is changed into a soluble chromite, just as aluminium hydroxide forms soluble aluminates. Unlike aluminates, however, the chromites are changed back into chromic hydroxide by boiling. Other chromic salts are chromic chloride ($CrCl_3$), chromic sulphate ($Cr_2(SO_4)_3$), and potassium chromium sulphate or chrome alum ($K_2Cr_2(SO_4)_4 . 24\ H_2O$). The valence of chromium in chromic compounds is three.

**Chromites** may be regarded as salts of an acid having the composition corresponding to $HCrO_2$; native chromite ($FeCr_2O_4$ or $Fe(CrO_2)_2$) is an iron salt of this acid.

**Chromates** and **dichromates** start theoretically from chromium trioxide ($CrO_3$). This is the anhydride of the hypothetical chromic acid ($H_2CrO_4$). When concentrated sulphuric acid is added to a saturated solution of potassium dichromate (or chromate), chromium trioxide ($CrO_3$) separates as long, bright red crystals, thus:—

| $K_2Cr_2O_7$ | + | $H_2SO_4$ | = | $2\,CrO_3$ | + | $K_2SO_4$ | + | $H_2O$ |
|---|---|---|---|---|---|---|---|---|
| Potassium Dichromate | | Sulphuric Acid | | Chromium Trioxide | | Potassium Sulphate | | Water |

It is sometimes called chromic acid, and is a vigorous oxidizing agent. The valence of chromium in chromates and dichromates is six; the radicals $CrO_4$ and $Cr_2O_7$ have the valence two.

**Miscellaneous.** — Chromium compounds yield several kinds of ions, *e.g.* the violet chromic ion ($Cr^{+++}$), the yellow chromate ion ($CrO_4^{--}$), and the red dichromate ion ($Cr_2O_7^{--}$).

**Molybdenum** (Mo), **Tungsten** (W), and **Uranium** (U) are rare metallic elements related to chromium. Most of their compounds have only scientific interest, though some have analytical or industrial uses. Ammonium molybdate ($(NH_4)_2MoO_4$) is used in the laboratory to determine the amount of phosphorus in fertilizers and iron. Tungsten is used to harden steel, and as the filament of electric light bulbs; sodium tungstate ($Na_2WO_4$) finds application in rendering cloth fireproof. Uranium compounds are obtained from uraninite and pitchblende, the latter mineral now being the chief source. The element forms many compounds and the important ones are the oxides, sodium uranate ($Na_2U_2O_7 \cdot 6\,H_2O$), and uranyl nitrate ($UO_2(NO_3)_2 \cdot 6\,H_2O$); from the nitrate other salts are prepared. Sodium uranate is sometimes called uranium yellow, and it is used to make uranium glass. Such glass is green by transmitted light and yellow by reflected light. Uranium is a radio-active element.

### Problems and Exercises

1. What is the per cent of chromium in (*a*) lead chromate ($PbCrO_4$), (*b*) chrome ironstone ($Fe(CrO_2)_2$), (*c*) chromic oxide ($Cr_2O_3$)?

2. How many grams of lead chromate can be made from 438 gm. of potassium dichromate?

3. Suppose 2.8338 gm. of chromium chloride ($CrCl_3$) yield 7.6919 gm. of silver chloride? What is the atomic weight of chromium, on the assumption that the atomic weights of chlorine and silver are 35.46 and 107.88 respectively?

4. Write the formulas of the following compounds, and calculate the per cent of chromium in each: Barium chromate, ammonium chromate, chromic nitrate, chromous chloride, lithium dichromate.

5. What is meant by the term *double salt* as applied to chrome alum?

### Radio-Activity

It was discovered about 1896 that uranium and its compounds affect a photographic plate and discharge an electroscope. Numerous experiments by Becquerel, Curie, Rutherford, and others showed that these effects are due to radiations not unlike X-rays and Röntgen rays. Furthermore, according to a reliable authority, "the results obtained by observations on uranium and its compounds indicate that this power of radiation belongs to the uranium itself, and that the radiations are emitted spontaneously without the aid of any outside agency." Other substances, especially radium compounds, possess similar properties, and, as stated in the preliminary discussion of radium, such substances are said to exhibit radio-activity. Soon after (1898) an extensive examination of many minerals showed that the element thorium and its compounds are radio-active, and more particularly that certain minerals containing uranium, especially pitchblende, are more radio-active than uranium itself. A radio-active substance was extracted from pitchblende by M. and Mme. Curie, and the elementary constitu-

MADAME CURIE

ent in it was named **radium**. Radium itself, as already mentioned, has recently been isolated, but whenever the word *radium* is used, a radium compound, usually the bromide, is meant. The purified radium compound prepared by the Curies was found to be about a million times more radio-active than uranium.

Radio-active substances give off three types of radiations, or rays, which are designated $\alpha$-rays, $\beta$-rays, and $\gamma$-rays. To the $\alpha$-rays are ascribed most of the electrical effects, such as discharging an electroscope. The $\beta$-rays are the most efficient in affecting a photographic plate. The $\gamma$-rays differ from the others in possessing the least electrical and photographic power, and in being the most penetrative of all three; these are similar to X-rays. It has been found that $\alpha$- and $\beta$-rays consist of electrically charged particles moving with a tremendous velocity. The $\alpha$-particles bear a positive charge of electricity and have about twice the weight of a hydrogen atom. The $\beta$-rays carry a negative charge of electricity, and their weight is much less than that of $\alpha$-particles, varying according to different authorities from $\frac{1}{1000}$ to $\frac{1}{2000}$ of the weight of a hydrogen atom. These rays behave like the cathode rays developed in a vacuum tube, and are identical with electrons or corpuscles, *i.e.* with the subatomic particles of the physicist. The $\gamma$-rays are not material particles, but pulses in the ether.

If the emission of these rapidly moving particles in the $\alpha$- and $\beta$-rays is retarded by metals or some other substances, or if the particles are retained within the radio-active substance itself, some of their kinetic energy is transformed into heat. A mass of radium compound is always appreciably hotter than its surroundings. One gram of radium in combination develops spontaneously about 100 calories of heat per hour.

It has been found by experiment that in radio-active

substances continuous changes are going on, which give rise to new substances entirely distinct from one another. The new substances are not always stable, however, each decaying, so to speak, in its own definite period of time. Thus, uranium gives a substance called uranium X, and radium gives a gaseous substance called radium emanation; according to some authorities there is an intermediate substance between these two derivatives. The radium emanation likewise decays and yields a series of new radio-active substances. The series as far as completed is as follows : —

| | |
|---|---|
| Uranium | Radium B |
| ↓ | ↓ |
| Uranium X | Radium C |
| ↓ | ↓ |
| Ionium | Radium D |
| ↓ | ↓ |
| Radium | Radium E |
| ↓ | ↓ |
| Emanation | Radium F |
| ↓ | ↓ |
| Radium A | Radium G |

Similar series exist in the case of thorium and actinium. On the basis of these and other observations, too extensive to give here, it is believed that radium is being produced continuously from uranium, and that radium in turn produces radium emanation, and so on. Again, it has been shown experimentally by Ramsay and others that helium is one of the products resulting from the decay of radium emanation.

The whole subject of radio-activity is being assiduously investigated, and possibly some of our present notions will undergo revision as facts accumulate. However, certain facts stand out clearly, viz. that uranium, thorium, radium,

and possibly other elements, are undergoing spontaneous decomposition, that helium and possibly other elements are formed by the decay of elements having a higher atomic weight, that the atom as postulated by chemists is unstable and tends to assume more stable forms, and that enormous quantities of energy are involved in these transformations.

# CHAPTER XXXIII

## Iron, Nickel, and Cobalt

### Iron

Iron is the most useful of all metals. It has been known for ages, though not so long as the other common metals, and has been indispensable in the development of the human race.

The symbol of iron, Fe, is from the Latin word *ferrum*. From *ferrum* are derived the words *ferric* and *ferrous*, which give the corresponding forms ferri- and ferro- (found in such words as ferricyanide, ferrocyanide, etc.).

**Occurrence of Iron.** — Uncombined iron is found only in meteorites, which fall upon the earth from remote regions in space, and in certain volcanic rocks. Combined iron is abundant and widely distributed, constituting about 4.5 per cent of the earth's crust. It is found in most rocks and many minerals, in the soil, in springs and natural waters, in chlorophyll (the green coloring matter of plants), and in hæmoglobin (the red coloring matter of the blood). The chief ores of iron are hematite ($Fe_2O_3$), limonite ($2\,Fe_2O_3 . 3\,H_2O$), magnetite ($Fe_3O_4$), and siderite ($FeCO_3$). These ores often contain some impurity, such as silica, clay, calcium or magnesium carbonate, and small quantities of compounds of sulphur, phosphorus, and manganese.

Other abundant native compounds of iron are pyrites ($FeS_2$), pyrrhotite (varying from $Fe_6S_7$ to $Fe_{11}S_{12}$), and the copper-iron sulphides (chalcopyrite, $CuFeS_2$, and bornite, $Cu_3FeS_3$). They are not used to any extent as a source of iron.

The United States leads the world in the production of iron ore, the annual output for the last few years being about 50,000,000 tons. This vast quantity comes from twenty-five different states, but the bulk is mined in Minnesota, Michigan, Alabama, Wisconsin, Tennessee, Virginia, West Virginia, and Colorado. The most abundant ore is the red hematite, which comes chiefly from the Lake Superior region (Fig. 79); large quantities are mined in Alabama and Tennessee. The latter states, together with Virginia and West Virginia,

Fig. 79. — Deposits of iron and copper near Lake Superior. The iron regions, known as ranges, are Marquette (1), Menominee (2), Gogebic (3), Vermilion (5), Mesabi (6). No. 4 is the copper region.

furnish most of the limonite or brown iron ore. Pennsylvania, New Jersey, and New York contribute most of the magnetite, though some is mined also in Michigan. The carbonate ores, which constitute less than 1 per cent of the output, come mainly from Ohio, Maryland, and New York. Improvements in the machinery and methods used in mining and transporting iron ore have reduced its cost and facilitated its production. Thus, at an incredibly small expense, ore from the Lake Superior region is raised from open pits by steam shovels, dumped into large cars, carried to shipping ports on the lakes, dumped again into huge bunkers, dropped down chutes into big freight steamers (many of which hold 6000 tons) which carry it to South Chicago and Milwaukee, though over two thirds is

received at ports on the south shore of Lake Erie and forwarded by rail to Pittsburg, Pennsylvania. This city is the center of iron and steel industries. Birmingham, Alabama, is the center of the industry in the South, because near it the necessary ore, coal, and limestone are conveniently located.

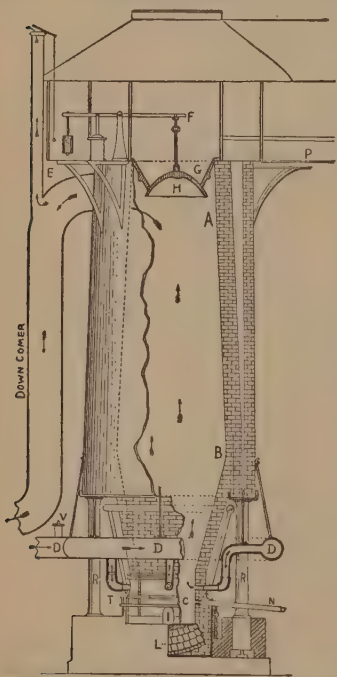



FIG. 80. — Blast furnace: *A*, throat; *B*, bosh; *C*, crucible where the melted iron collects; *D*, pipes for hot-air blast; *E*, escape pipe for gases which do not escape through the "down comer"; *G*, cup; *H*, cone; *N*, trough for drawing off slag; *T*, tuyere; *I*, hole through which iron is withdrawn.

**Metallurgy of Iron.** — Iron is extracted most easily from its oxides. Therefore, the ore, unless it is very pure hematite, is first crushed and roasted to change it into ferric oxide ($Fe_2O_3$) as far as possible. Thus prepared, the ore is mixed with coke and limestone and smelted in a blast furnace. The carbon reduces the oxide to metallic iron, which collects as a liquid at the bottom of the furnace beneath the slag formed by the limestone and impurities. The blast furnace (Fig. 80) is a huge circular tower, from forty to ninety feet high, and about thirteen feet in diameter at the largest part. It is built of iron and lined with fire brick. Pipes near the bottom, called tuyeres, allow large quantities of hot air to be forced into the furnace

up through the contents, thereby producing the high temperature required in the smelting; while another pipe at the top not only permits the escape of the hot gaseous products, but conducts them into a series of pipes which lead to different parts of the plant, where the hot gases are utilized to heat the air which is blown through the furnace. The blast pipes correspond to the bellows used by the blacksmith, and the exit pipe to the chimney, except that gases escaping through chimneys are usually wasted.

When the blast furnace has been heated to the proper temperature, or is already in operation, the mixture or charge is carried to the top by machinery and introduced into the furnace by dumping it upon the cone-shaped cover; the weight lowers the cover, which flies back tightly into place after the materials roll into the furnace. The charge consists of the proper mixture of ore, fuel, and flux. The ore, as stated above, is usually hematite. The fuel is coke, or coke mixed with coal. The flux varies with the impurities in the ore; thus, it is limestone if the ore contains silica or clay, but sand if the impurities are calcium or magnesium compounds. It is usually limestone. The object of the flux is to remove the impurities (just mentioned) from the charge in the form of readily fusible silicates called **slag**. As the smelting proceeds, the contents of the furnace slowly descend and are changed into gases, iron, and slag. The gases rise through the mass and escape by pipes, the solids become pasty at first and then liquid, the iron finally dropping through the slag into the crucible at the bottom of the furnace, where both are drawn off through separate openings. Fresh charges of definite weight and proportions are added at regular intervals, and the whole operation continues without interruption for months or even years.

The iron from the furnace is usually poured into molds of sand or iron and allowed to solidify. Such iron is called

**pig iron** or **cast iron.** In some plants the molten iron is run directly from the blast furnace into huge vessels called converters and made at once into steel (see below); in other plants it is kept molten in huge tanks until needed.

The chemical changes involved in the metallurgy of iron are numerous. In general, the iron oxide is reduced to metallic iron largely by carbon monoxide. The carbon of the fuel at first forms carbon dioxide with the oxygen of the air blast. But the dioxide is soon reduced by the hot carbon to the monoxide, which interacts with the ore, thus: —

$$\underset{\text{Ferric Oxide}}{3\,Fe_2O_3} + \underset{\text{Carbon Monoxide}}{CO} = \underset{\text{Ferrous-ferric Oxide}}{2\,Fe_3O_4} + \underset{\text{Carbon Dioxide}}{CO_2}$$

$$Fe_3O_4 + CO = \underset{\text{Ferrous Oxide}}{3\,FeO} + CO_2$$

$$FeO + CO = Fe + CO_2$$

At this stage the ore, though not wholly reduced, becomes soft and porous, and as the mass sinks into the hottest part of the furnace the reduction is completed, thus: —

$$FeO + C = Fe + CO$$

The iron now combines with a small percentage of carbon, melts, and sinks through the molten slag. This iron contains small amounts of carbon, silicon, manganese, phosphorus, and sulphur.

**Varieties of Iron.** — The iron we use and speak of is not pure iron, but a mixture or compound of iron with other elements, chiefly carbon. It is customary to speak of three varieties of iron, — cast iron, wrought iron, and steel. This classification is based chemically upon the per cent of carbon they contain, though their physical properties are also modified by the presence of silicon, phosphorus, sulphur,

and manganese, as well as by the method of manufacture. The different varieties are closely related, and pass easily and gradually into each other. Commercially, there are several kinds of cast iron and many kinds of steel.

**Cast Iron** is the most impure variety. It contains, besides carbon, the impurities already mentioned. The carbon varies from 3 to 5 per cent, the silicon and manganese are each about 3 per cent, while the proportion of phosphorus and sulphur is small. Cast iron has a crystalline structure and is brittle. If most of the carbon is combined with the iron, the metal is called white cast iron. But if the molten metal cools slowly, much of the carbon remains uncombined as hard crystals known as graphite carbon, and the color of the iron is gray; this kind is gray cast iron. It is softer than the white variety, and melts at a lower temperature. Although cast iron is brittle, it will withstand great pressure. Owing to its crystalline structure, it cannot be welded or forged; that is, hot pieces cannot be united, nor be shaped by hammering. But it is extensively used to make castings. This is the kind of iron used in an ordinary iron foundry. The iron, which melts at about 1200° C. (depending upon the impurities), is heated in a furnace similar to a blast furnace, and when molten is poured into sand molds of the desired shape. Stoves, pipes, pillars, railings, parts of machines, and many other useful objects are made of cast iron.

Cast iron containing 5 to 20 per cent of manganese is called spiegel iron, while ferro-manganese contains from 20 to 85 per cent of manganese. Both are used in making steel.

**Wrought Iron** is the purest variety of commercial iron. It contains not more than 0.5 per cent of carbon and sometimes only 0.06 per cent, the average being 0.15 per cent. It is tough, malleable, and fibrous, and can be bent. Unlike cast iron, it does not withstand pressure, but it will sustain

great weight. An iron wire will sustain the weight of nearly a mile of itself. Wrought iron melts at such a high temperature (1550° to 2000° C.) that it is not used for casting; it softens at a relatively low temperature (about 1000° C.), can be forged and welded, and is often called malleable iron. It may be seen undergoing these operations in a blacksmith's shop. It can also be rolled into sheets and plates and drawn into fine wire; in these forms the metal is very strong. Wrought iron is made into wire, sheets, rods, nails, spikes, bolts, chains, anchors, horseshoes, tires, and agricultural implements. It is less important than formerly, since it is being largely replaced by steel.

Wrought iron is made from cast iron by burning out most of the impurity. Cast iron together with a little scrap iron and flux is melted in a furnace, much like a reverberatory furnace, lined on the bottom and sides with iron ore (ferric oxide, $Fe_2O_3$). The impurities are oxidized partly by the oxygen of the air, but mainly by the oxygen of the iron oxide; the silicon, phosphorus, sulphur, and manganese pass off as slag, and most of the carbon escapes as an oxide, though a small amount remains in the iron. As these elements are removed, the mass becomes pasty, owing to the higher melting point of the pure iron. It is now stirred vigorously, or "puddled." At the proper time lumps called "blooms" are removed and hammered, or more often rolled between ponderous rollers. This operation removes the slag, and if the rolling is repeated, the quality of the iron is improved; the final rolling often leaves the iron in the shape desired for market.

**Steel** is usually intermediate between cast iron and wrought iron as far as its proportion of carbon is concerned. Many grades of steel are manufactured, and their physical prop-

erties do not depend merely upon the presence of a small proportion of carbon and other elements, especially phosphorus, silicon, and certain metals, but to a considerable extent upon the method of manufacture and subsequent treatment. Considered from the standpoint of composition, it may be said that in general the higher the percentage of carbon, the harder the steel. In soft or mild steel the carbon is seldom more than .2 per cent, while in hard steel the amount may be as high as 1 per cent.

**Manufacture of Steel.** — The aim in the manufacture of steel is to prepare a product containing little or no sulphur, phosphorus, and silicon, but the desired proportion of carbon. This is accomplished by several processes, viz. the Bessemer, open-hearth, crucible, and cementation.

(1) The **Bessemer process** is the one in most general use. It was devised about 1860, and has practically revolutionized steel making. The process consists in burning out the impurities in cast iron by forcing air through the molten metal, and then adding just enough iron of known composition to give the desired proportion of carbon. The operation is carried on in a converter (Fig. 81). This is a huge, pear-shaped vessel, supported so that it can be tipped into different positions; it is also provided with holes (*C*, *C*, *C*) at the bottom, through which a powerful blast of air can be blown. It is made of thick wrought-iron plates, and is lined with an infusible mixture, usually rich in silica. The converter when in use is swung into a horizontal position (*A*), and five to twenty tons of molten pig iron are poured in, often directly from the blast furnace. The air blast is turned on and the converter is swung back to a vertical position (*B*). As the air is forced in fine jets through the molten metal, the temperature rises, and the carbon, silicon, and manganese are oxidized. The carbon forms carbon mon-

oxide, which burns at the mouth of the converter, while the other oxides pass into the slag. This oxidation generates enough heat to keep the metal melted, and no fuel need be used. As soon as the impurities have been burned out, sufficient spiegel iron or ferromanganese is added to furnish the proper amount of carbon and manganese. By adding

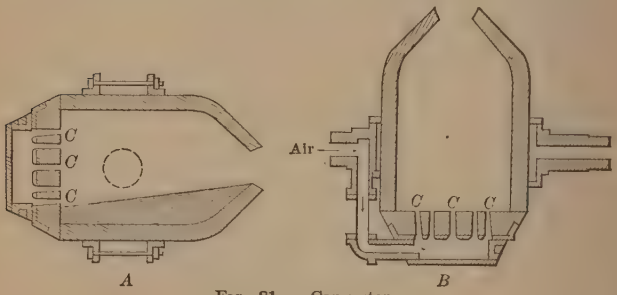



Fig. 81. — Converter.

spiegel iron of known composition, Bessemer steel of any desired grade is produced. After the completion of the operation, which takes about twenty minutes, the metal is poured from the converter into molds to cool. These cold blocks of steel are called ingots.

In the Bessemer process, as described in the preceding paragraph, sulphur and phosphorus are not removed from the steel. Both are objectionable impurities; sulphur makes steel brittle when hot, and phosphorus makes it brittle when cold. The **Thomas-Gilchrist process** (or basic process) is a modification of the Bessemer process by which the sulphur and phosphorus can be removed in the slag. The converter in this process is lined with burned dolomite (*i.e.* practically a mixture of lime and magnesia), called a basic lining; lime is also added to the charge of pig iron, and the

air blast is continued a little longer than in the Bessemer process; otherwise the operations are the same. The carbon passes off as usual, and the oxides of phosphorus, silicon, and sulphur combine with the basic constituents of the lining to form a slag. This lining, after use, is known as Thomas slag; it is utilized as a fertilizer on account of its phosphorus content.

(2) In the **Siemens-Martin or open-hearth process** cast iron, or a mixture of cast iron, scrap iron, and iron ore, in

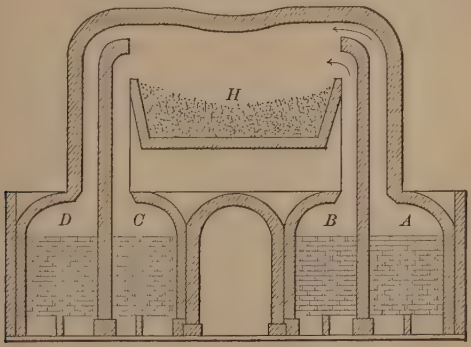



FIG. 82. — Open-hearth furnace.

proper proportions, is melted by hot gases in a special kind of furnace called an open-hearth furnace (Fig. 82). The receptacle, or hearth (*H*), in which the charge is melted, is lined with sand or burned dolomite, as in the Bessemer process, thereby permitting the more or less complete removal of all the impurities. At the base of the furnace are duplicate sets of checkerwork (*A*, *B* and *C*, *D*). As the hot gases pass through *A*, *B* to the chimney, they heat the checkerwork. The fuel gas is then passed through *B* and air through *A*. The mixture of air and gas burns and pro-

duces a much higher temperature on the hearth than if the gaseous mixture were cool. The oxidizing flame passes over the charge on the hearth (*H*), oxidizing some of the impurities and keeping the mass at such a temperature that other impurities form a slag with the lining. Meanwhile the hot products of combustion and the unused gases are passed through the checkerwork *C*, *D* and heat it. The fuel gas and air are then made to pass through this checkerwork to the hearth and out over the other checkerwork (*A*, *B*) to the chimney. Thus the process is alternated, one checkerwork being cooled as the other is heated, and *vice versa*. It is only by this regenerative process, as it is called, that enough heat is obtained to keep the charge melted as it becomes purer and purer. The charge is heated from six to twelve hours; when a test shows that the metal contains the desired proportion of carbon, ferromanganese is added, and the steel is quickly poured into molds and allowed to cool into ingots. Subsequently the ingots of this kind of steel (as well as of other kinds) are reheated, rolled, and cut into lengths of the proper size and shape, being then known as billets. The open-hearth process requires a special furnace and gas plant, and is more expensive than the Bessemer process, since it takes much longer. But it is easily controlled, and yields a tough, elastic steel, which is excellent for bridges, large machines, large guns, and gun carriages. The production of the open-hearth steel has increased rapidly in the last few years.

(3) In the **crucible process** wrought iron is melted with charcoal in graphite or clay crucibles. During the melting, which lasts three or four hours, the iron is slowly changed into steel by absorbing the proper proportion of carbon.

(4) In the **cementation process** wrought iron and carbon are heated in fire-brick boxes for several days. The transformation is the same as in the crucible process.

The four processes of making steel, just described, provide many grades which permit its use for countless purposes. In recent years **special steels** have been made by adding to steel small quantities of other metals, such as nickel, chromium, molybdenum, tungsten, silicon, and manganese. Such steels differ somewhat in special properties, but all are characterized by extreme hardness, toughness, and strength. The metals are sometimes added directly to the molten steel, but more often in the state of an alloy of iron. These alloys contain varying but known percentages of the constituents, and are called ferrochrome, ferrosilicon, ferrotungsten, etc.

The **important properties of steel** are numerous. It is fusible and malleable, and can be forged, welded, and cast. It is harder, stronger, and more durable than pure iron, and is therefore more serviceable. But its most valuable property is the varying hardness which it may be made to acquire. If steel is heated very hot and then suddenly cooled by immersion in cold water or oil, it becomes brittle and very hard. But if heated and cooled slowly, it becomes soft, tough, and elastic. All grades of hardness may be obtained between these extremes. And if the hardened steel is reheated to a definite temperature, determined approximately by the color the oxidized metal assumes, and then properly cooled, a definite degree of hardness and elasticity is obtained. This last operation is called **tempering**.

**Uses of Steel.** — Steel is now used instead of iron for many purposes. High buildings, bridges, rails, cars, locomotives, battleships electrical machinery, boilers, agricultural implements, wire nails, rods, hoops, tin plates, and castings of all kinds consume vast amounts of Bessemer and open-hearth steel. Crucible, cementation, and special steels are used in making springs, tools, cutlery, pens, and needles.

**Properties of Pure Iron.** — Chemically pure iron can be obtained as a black powder by reducing the oxide with hydrogen. Recently very pure massive iron has been prepared electrolytically from a solution of ferrous and ammonium sulphates. The purest commercial form is the wrought iron used for piano wire. Pure iron is a silvery white, lustrous metal. It is softer than ordinary iron, but melts at a higher temperature (about 1500° C.). The specific gravity is about 7.8. It is attracted by a magnet, but soon loses its own magnetism. Dry air has no effect upon iron, but moist air rusts it. The rusting of iron is a complex process and is differently interpreted. Iron rust has a variable composition, but its essential constituent is believed to be a ferric hydroxide. Rusting proceeds rapidly, because the film of rust is not compact enough to protect the metal. Like many metals, iron readily interacts with dilute acids, and as a rule hydrogen and ferrous compounds are the products. Sometimes the hydrogen is mixed with gaseous hydrocarbons and disagreeably smelling compounds of sulphur and phosphorus evolved from the impurities in the iron.

With nitric acid various products result, according to the conditions, — ferrous nitrate and ammonium nitrate if the acid is cold, but ferric nitrate and oxides of nitrogen if the acid is warm. If a clean iron wire is dipped into fuming nitric acid and then into ordinary nitric acid, no action is apparent. The iron is said to be passive. This peculiar fact has not been adequately explained. Steam and hot iron interact thus: —

$$\underset{\text{Iron}}{3\,Fe} + \underset{\text{Water}}{4\,H_2O} = \underset{\text{Iron Oxide}}{Fe_3O_4} + \underset{\text{Hydrogen}}{4\,H_2}$$

The film of the oxide ($Fe_3O_4$), unlike iron rust, adheres firmly and protects the iron from further oxidation.

**Compounds of Iron.** — Iron forms two important series of compounds, — ferrous and ferric. They are analogous

to cuprous and cupric, mercurous and mercuric compounds. The valence of iron is two in ferrous compounds and three in ferric. Ferrous compounds in an acid solution pass into the corresponding ferric compound by the action of oxidizing agents, *e.g.* oxygen, nitric acid, potassium chlorate, potassium permanganate, and chlorine. Conversely, ferric compounds are reduced to the ferrous by reducing agents, *e.g.* hydrogen, hydrogen sulphide, sulphur dioxide, and stannous chloride. The passage from one series to the other occurs easily, especially from ferrous to ferric. The oxidation and reduction of iron compounds illustrates typically the broad use of these terms. Oxygen is not necessarily involved. Thus, ferrous and ferric chlorides pass readily into each other by the addition or removal of chlorine. The two processes are general and mutual, and may be summarized as follows: (*a*) Oxidation is the chemical addition of oxygen or any other negative element, such as chlorine; reduction is the removal of oxygen or any other negative element. (*b*) From the standpoint of the ionic theory, oxidation is the addition of positive electricity, and reduction the withdrawal. Thus, when ferrous chloride solution becomes ferric chloride upon the addition of chlorine, the ferrous ions ($Fe^{++}$) become ferric ions ($Fe^{+++}$), while the electrically neutral chlorine molecules, having become ions, lose positive electricity, *i.e.* they undergo reduction. (*c*) Occasionally, oxidation is spoken of as occurring when the valence is raised, and reduction when the valence is lowered. For instance, in the change from ferrous to ferric compounds the valence of iron is raised from two to three, while by the reduction of ferric to ferrous the valence is lowered from three to two. (Compare interaction of mercuric chloride and stannous chloride.)

**Oxides and Hydroxides of Iron.** — Iron forms three oxides.

**Ferrous oxide** (FeO) is an unstable black powder. **Ferric oxide** ($Fe_2O_3$) occurs native in many varieties as hematite — the most abundant ore of iron. It can be prepared by heating ferrous sulphate or ferric hydroxide. Large quantities are manufactured from the ferrous sulphate obtained as a by-product in the cleansing of the iron used in making galvanized and tinned ware. It is sold under the names rouge, crocus, and Venetian red, and is used to polish glass and jewelry and to make red paint. **Ferrous-ferric**, or **ferroso-ferric**, oxide (magnetic oxide of iron, $Fe_3O_4$), occurs native as magnetite; if noticeably magnetic, it is called loadstone. It is produced as a black film or scale by heating iron in the air; heaps of it are often seen beside the anvil in a blacksmith's shop. The firm coating of this oxide formed by exposing iron to steam protects the metal from further oxidation. **Ferrous hydroxide** ($Fe(OH)_2$) is a white solid formed by the interaction of a ferrous salt and an alkali, such as sodium hydroxide. Exposed to the air, it soon turns green, and finally brown, owing to the formation of ferric hydroxide. **Ferric hydroxide** ($Fe(OH)_3$) is a reddish brown solid, formed by the interaction of an alkaline hydroxide (*e.g.* ammonium or sodium hydroxide) and a ferric salt. The freshly prepared compound is an antidote for arsenic.

**Ferrous Sulphate**, $FeSO_4$, is a green salt obtained by the interaction of iron (or ferrous sulphide) and dilute sulphuric acid, and is a by-product in several large industries (*e.g.* see Ferric Oxide). It is also prepared on a large scale by oxidizing iron pyrites ($FeS_2$). This is accomplished simply by roasting, or more often by exposing heaps of pyrites to moist air; the mass is extracted with water containing scrap iron and a small proportion of sulphuric acid, and large light green crystals are obtained from the solution. The crystallized salt ($FeSO_4 . 7\,H_2O$) is also called green vitriol or

**copperas.** Exposed to the air, ferrous sulphate effloresces and oxidizes. Large quantities are used as a mordant in dyeing silk and wool, as a disinfectant and a wood preservative, and in manufacturing ink, bluing, pigments, leather, varnish, and mottled soaps. Much black writing ink is made essentially by mixing ferrous sulphate, nutgalls, gum, and water. A mixture of lime and ferrous sulphate is used as a coagulant in purifying water and sewage.

**Ferric Sulphate**, $Fe_2(SO_4)_3$, is formed by oxidizing an acid solution of ferrous sulphate with nitric acid. When ferric sulphate solution is mixed with the proper quantity of potassium (or ammonium) sulphate, **iron alum** ($K_2SO_4 . Fe_2(SO_4)_3 . 24\,H_2O$ or $K_2Fe_2(SO_4)_4 . 24\,H_2O$) is formed. It is a pale violet, crystalline solid, which has properties like ordinary alum. Iron alum is used chiefly as a mordant.

**Iron Sulphides.** — There are two iron sulphides. Commercial **ferrous sulphide** (FeS) is a black, brittle, metallic-looking solid, but the pure compound is yellow and crystalline. It is also obtained as a fine black precipitate by the interaction of a dissolved ferric or ferrous salt and ammonium sulphide, though not by hydrogen sulphide. It is made on a large scale by fusing a mixture of iron and sulphur. Its chief use is in preparing hydrogen sulphide. **Ferric sulphide** (iron disulphide, iron pyrites, pyrite, $FeS_2$) is one of the commonest minerals. It is a lustrous, metallic, brass-yellow solid. Crystals of pyrites, found in many rocks, are often mistaken for gold — hence the popular name, "fool's gold." It is valueless as an iron ore, but large quantities are used as a source of sulphur in making sulphuric acid. Over one and a half million tons are annually consumed in the sulphuric acid industry.

**Iron Chlorides.** — When iron interacts with hydrochloric acid, **ferrous chloride** ($FeCl_2$) is formed in solution. **Ferric chloride** ($FeCl_3$) is readily prepared by passing chlorine gas into a solution of ferrous chloride. It is a dark, lustrous, crystalline solid; but owing to its extreme deliquescence, it is usually sold as a solution, which is a brown liquid. When treated with nascent hydrogen or another reducing agent, ferric chloride is changed into ferrous chloride.

**Ferrous Carbonate,** $FeCO_3$, occurs native as the iron ore siderite, clay ironstone, or spathic iron ore. The typical variety is light yellow or brown, lustrous, crystalline, and not very hard; but many kinds are impure, and the properties vary. It is slightly soluble in water containing carbon dioxide, and is therefore found in some mineral springs. (See Chalybeate Waters.) Like all carbonates, it yields carbon dioxide with warm hydrochloric acid.

**Iron Cyanides.** — Iron and cyanogen $(CN)_2$, with or without potassium, form several compounds. The most important is **potassium ferrocyanide** ($K_4Fe(CN)_6$). It is a lemon-yellow, crystalline solid, containing three molecules of water of crystallization. Unlike most cyanogen compounds, it is not poisonous. Its commercial name is yellow prussiate of potash. It is manufactured by fusing together iron filings, potassium carbonate, and nitrogenous animal matter (such as horn, hair, blood, feathers, and leather). The mass is extracted with water, and the salt is separated by crystallization. In Germany this salt is manufactured from the iron oxide which has been used to purify illuminating gas. Large quantities are used in dyeing and calico printing, and in making bluing and potassium cyanogen compounds. **Potassium ferricyanide** ($K_3Fe(CN)_6$) is a dark red, crystalline solid, containing no water of crystallization. It is often called red prussiate of potash. It is manufactured

by oxidizing potassium ferrocyanide with potassium permanganate or chlorine, thus:—

$$\underset{\text{Potassium Ferrocyanide}}{2\ K_4Fe(CN)_6} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Potassium Ferricyanide}}{2\ K_3Fe(CN)_6} + \underset{\text{Potassium Chloride}}{2\ KCl}$$

It is very soluble in water, forming a yellow, unstable solution. In alkaline solution it is a vigorous oxidizing agent, and finds extensive use in dyeing. It is also used as one of the ingredients of the sensitive coating of "blueprint" paper.

The valence of the radical $Fe(CN)_6$ is three in ferricyanides and four in ferrocyanides.

Ferrous salts and potassium ferricyanide interact in solution and produce **ferrous ferricyanide** ($Fe_3(Fe(CN)_6)_2$). This is a blue solid and is often called Turnbull's blue. But ferrous salts produce with potassium ferrocyanide a white precipitate (ferrous ferrocyanide) which quickly oxidizes to a complex blue compound. Ferric salts interact with potassium ferrocyanide and produce **ferric ferrocyanide** ($Fe_4(Fe(CN)_6)_3$). This is a dark blue solid, and is called Prussian blue or Berlin blue. Ferric salts produce no precipitate with potassium ferricyanide. Prussian blue is extensively used in dyeing and calico printing, and in making bluing. The above reactions, which allow ferrous and ferric salts to be distinguished, may be summarized as follows: —

| Cyanide | Ferrous Salt | Ferric Salt |
|---|---|---|
| Ferrocyanide | Whitish precipitate | Prussian blue |
| Ferricyanide | Turnbull's blue | No precipitate |

Besides the above tests, potassium sulphocyanate (KCNS) produces a blood-red solution of **ferric sulphocyanate** ($Fe(CNS)_3$) with ferric salts, but leaves ferrous salts unchanged. The tests for iron are thus numerous and specific.

**Miscellaneous.** — Iron compounds yield several kinds of ions, *e.g.* the ferrous ion ($Fe^{++}$) and the ferric ion ($Fe^{+++}$); each is colorless, though the former appears delicate green and the latter very pale yellow, owing to traces of other substances. Complex ions are $Fe(CN)_6^{----}$ and $Fe(CN)_6^{---}$. The atomic weight of iron is 55.85.

## Nickel

**Nickel**, Ni, occurs combined with arsenic or with arsenic and sulphur as niccolite (NiAs) and nickel glance (NiAsS). Small amounts of metallic nickel are found in meteorites. The ores which furnish most of the commercial nickel are the nickel-bearing iron sulphides of the Sudbury district, Canada, and the silicate of nickel and magnesium (garnierite) found in New Caledonia.

**Preparation and Properties.** — Nickel is obtained from its ores by a complicated smelting or electrolytic process. It is a white, hard metal. It is ductile and tenacious. It takes a brilliant polish and does not tarnish in dry air, though in moist air it tarnishes very slowly. Like iron, it is attracted by a magnet.

**Uses of Nickel.** — For many years it has been used as one ingredient of the small coins of several countries. The per cent of nickel varies from 12 in the United States cent to 25 in the five-cent piece. German silver contains from 15 to 25 per cent of nickel, the rest being copper and zinc. Large quantities of nickel are used to coat or plate other metals, especially iron and brass. The nickel plating is done by electrolysis, as in the case of silver and gold plating, though the electrolytic solution used is a sulphate of nickel and ammonium ($(NH_4)_2SO_4 . NiSO_4$) — not a cyanide, as in the other cases. The deposit of nickel is hard, brilliant,

and durable. Nickel becomes malleable if a little magnesium or aluminium is added to the molten metal, and sheets of iron covered with such nickel are made into household utensils. **Nickeloid** is a nickel-plated sheet zinc. Its attractive appearance and non-corrosive property adapt it for the manufacture of reflectors, refrigerator linings, bath tubs, show cases, and signs. Nickel is used in the manufacture of nickel steel. This contains varying proportions of nickel. Large quantities are used for burglar-proof safes, the armor plates and turrets of battleships, and for the parts of machinery designed to withstand continuous wear and severe shocks.

**Compounds of Nickel.** — Nickel forms two series of compounds — the nickelous and the nickelic. The valence of nickel is two in the nickelous compounds and three in the nickelic. The nickelous compounds are the more common. Many nickel salts are green. The apple-green **nickelous hydroxide** ($Ni(OH)_2$) is formed by the interaction of an alkali and a dissolved nickel salt. **Nickelous sulphide** (NiS) is obtained as a black precipitate by the interaction of ammonium sulphide and a dissolved nickel salt. **Nickelous sulphate** ($NiSO_4$) and **nickelous chloride** ($NiCl_2$) are the usual commercial salts. **Nickel carbonyl** ($Ni(CO)_4$) is prepared by passing carbon monoxide over finely divided nickel. It is a volatile, colorless liquid which boils at 43° C. The vapor is poisonous and decomposes at 150°–180° C. into metallic nickel and carbon monoxide. This compound has a technical application in one method of preparing pure nickel. **Ammonium nickelous sulphate** ($(NH_4)_2SO_4 . NiSO_4$) was mentioned in the preceding paragraph.

**Tests for Nickel.** — The formation of the green nickelous hydroxide is a distinctive test. Nickel compounds color

a borax bead brown in the oxidizing flame and gray in the reducing flame.

**Miscellaneous.** — Nickelous salts yield a green ion ($Ni^{++}$). The atomic weight of nickel is 58.68.

## Cobalt

**Cobalt**, Co, generally occurs combined with arsenic or arsenic and sulphur as smaltite ($CoAs_2$) and cobaltite (CoAsS), which are usually associated with the corresponding nickel compounds.

**Preparation and Properties.** — Cobalt is obtained as a powder by reducing its oxide with hydrogen or as a coherent mass by the aluminothermic method. It is a white metal with a faint reddish tinge. Like nickel, it takes a brilliant polish. It is less magnetic than iron. Metallic cobalt has few uses.

**Compounds of Cobalt.** — Cobalt, like nickel, forms two series of compounds — the cobaltous and the cobaltic. The valence of cobalt is two in cobaltous compounds and three in cobaltic. The cobaltous compounds are the more common, though many complex cobalt compounds are known. **Cobaltous sulphide** (CoS) is obtained as a black precipitate by the interaction of ammonium sulphide and a dissolved cobalt salt. **Cobaltous chloride** ($CoCl_2$) and **cobaltous nitrate** ($Co(NO_3)_2$) are red crystalline salts; they crystallize with six molecules of water of crystallization. When part or all of the water of crystallization is driven off, these salts become violet or blue. A complex cobalt compound known as **smalt**, or smalt blue, is used to decorate porcelain. It has a variable composition, but is essentially a cobalt silicate. Cobalt compounds color glass blue. Such glass transmits red, blue, and violet light, but not yellow, orange, and green,

so it is sometimes used to detect the violet potassium flame when masked by the yellow sodium flame.

**Tests for Cobalt.** — Cobalt compounds color a borax bead blue in both flames. Cobaltous compounds when mixed with potassium nitrite and acetic acid form a yellow-white precipitate of **potassium cobaltinitrite** ($K_3Co(NO_2)_6$), thereby distinguishing cobalt from nickel. When compounds of aluminium are moistened with cobaltous nitrate solution and heated in a blowpipe flame, the mixture finally becomes a blue crust-like mass; zinc compounds produce a green mass under similar treatment.

### Problems and Exercises

1. Calculate the percentage composition of (*a*) ferric oxide, (*b*) ferrous sulphate, (*c*) ferrous sulphide (FeS).

2. If 1.586 gm. of iron form 2.265 gm. of ferric oxide, what is the atomic weight of iron? (Equation is $2\,Fe + 3\,O = Fe_2O_3$.)

3. What volume of oxygen (under standard conditions) is used in the oxidation of 100 gm. of ferrous oxide to ferric oxide?

4. What volume of hydrogen at 13° C. and 780 mm. is needed to reduce 63 gm. of ferric oxide to metallic iron?

5. Calculate the percentage composition of the three oxides of iron and show how they illustrate the law of multiple proportions.

6. A cobalt compound corresponding to nickel carbonyl is known. What is its formula?

7. Write the formulas of the following compounds by applying the principle of valence: Ferric acetate, ferric nitrate, ferrous bromide, nickelic sulphate, cobaltic nitrate.

8. Write the formulas of the following compounds and indicate the valence of each element: Potassium ferrocyanide, potassium ferricyanide, ferric ferrocyanide, ferrous ferricyanide, potassium cobaltinitrite.

9. Write the ionic equation for the oxidation of ferrous chloride to ferric chloride by chlorine.

10. Iron displaces copper from solutions of copper compounds. Write the chemical and the ionic equations representing this change.

## CHAPTER XXXIV

### Platinum and Associated Metals

**Occurrence of Platinum.** — Platinum occurs as the essential ingredient of platinum ore or so-called native platinum. The ore contains from 60 to 86 per cent of platinum. The other metals present are ruthenium, osmium, iridium, rhodium, and palladium. Iron, gold, and copper are also usually present. Only one native compound is known, viz. platinum arsenide (sperrylite, $PtAs_2$). These metals, like gold, are noble metals, *i.e.* they do not unite with oxygen at any temperature.

The word *platinum* is derived from *platina*, a form of the Spanish word *plata*, meaning silver, because native platinum was regarded as an impure ore of silver by the Spaniards, who first discovered it in South America about 1735. Platinum is now sometimes called by its old name *platina*.

**Preparation of Platinum.** — The platinum ore, which occurs as rounded grains or flattened scales in alluvial deposits, is first digested with mercury or dilute *aqua regia* to remove the gold, silver, and copper; and then with concentrated *aqua regia*, which changes all the platinum and a very little iridium into soluble compounds, leaving behind an alloy of iridium and osmium. From the clear solution the platinum and iridium are precipitated by ammonium chloride as compounds, which, on heating, yield the metals as a spongy mass. This **spongy platinum** is melted in a lime crucible with an oxyhydrogen flame or in the electric furnace, and hammered while hot into sheet platinum.

The very small amount of iridium is seldom removed from the metallic platinum.

**Properties and Uses of Platinum.** — Platinum is a lustrous, gray-white, soft metal. It is malleable and ductile, and usually appears in commerce in the form of wire, sheet, and dishes. Sheet platinum is cut into squares — the familiar platinum foil of the laboratory, or made into crucibles, dishes, and stills. Its use in these forms is due partly to its infusibility and partly to its resistance to acids and other corrosive chemicals. Although it is attacked by fused caustic alkalies, low melting metals, *aqua regia*, and a few other substances, it is practically indispensable in the chemical laboratory and is used in many chemical processes involving accurate analysis. Platinum is a good conductor of electricity, and large quantities are consumed in electrical apparatus, especially incandescent electric light bulbs. Short pieces of wire are fused into the glass at the base of the bulb and attached to the outside wires, thereby conveying the current to and from the carbon filament within. Platinum is the only metal thus far found which is perfectly adapted to this use, because it has the same coefficient of expansion as glass. Platinum has a specific gravity of about 21, which is higher than that of any known substance, except osmium and iridium. The melting point is over 1700° C. In the form of a black, porous mass it is called **spongy platinum**, and a still finer form is called **platinum black**. Both forms absorb large volumes of gases; and if a current of gas is directed against the metal, the gas often takes fire. Coherent platinum has the same property to a less degree, for it becomes red-hot if held in a stream of illuminating gas, and often ignites the gas. Finely divided platinum is used as the catalyzer in the contact method for making sulphuric acid. Platinum forms alloys with other metals,

and should never be heated with lead, similar metals, or their compounds, since the alloys have a low melting point. With iridium, however, it forms a very hard alloy of which the standard meters are made.

**Compounds of Platinum.** — Chloroplatinic acid ($H_2PtCl_6$) is a brownish, deliquescent solid prepared by treating platinum with *aqua regia* and evaporating the solution to crystallization. By carefully heating chloroplatinic acid in a current of chlorine, **platinum tetrachloride** ($PtCl_4$) is obtained; it resembles chloroplatinic acid in color but is not deliquescent. The acid forms salts, the best known being the yellow, crystalline potassium chloroplatinate ($K_2PtCl_6$) and ammonium chloroplatinate ($(NH_4)_2PtCl_6$).

The atomic weight of platinum is 195.0, and the valence is usually four.

The metals associated with platinum have limited uses. **Palladium** is used in chemical analysis to absorb hydrogen, and a native (as well as an artificial) alloy of iridium and osmium, called **iridosmine**, is used to tip gold pens. Iridosmine is often called **osmiridium**.

### Problems

1. A piece of platinum foil measuring 10.5 cm. by 1.5 cm. weighs .723 gm. Into how many pieces, each weighing 1 dg., may it be divided?

2. The specific heat of platinum is .0324. According to analysis, 35.5 gm. of chlorine unite with 48.6 gm. of platinum to form platinic chloride. What is (*a*) the atomic weight of platinum and (*b*) the formula of platinic chloride according to these figures?

# APPENDIX

1. **The Metric System** of weights and measures is used in physics and chemistry.

It is based on the **meter**. This is the unit of length, and it is a little longer than a yard. Its exact length is 39.37 inches — a number to remember. Lengths shorter than a meter are called decimeters, centimeters, and millimeters. Deci- means .1, centi- means .01, and milli- means .001. Lengths longer than a meter are called decameters, hectometers, and kilometers. Deca- means 10, hecto- means 100, kilo- means 1000. Notice that all these relations are decimal. Hence, a meter contains 10 decimeters, 100 centimeters, or 1000 millimeters. It is also evident that 10 millimeters equal 1 centimeter, 10 centimeters equal 1 decimeter, and that 1000 meters equal 1 kilometer. The millimeter, centimeter, decimeter, and meter are the denominations most frequently used in physical science to express length, though very long distances are expressed in kilometers. It is advisable to remember that —

1 decimeter = about 4 inches.
30 centimeters = about 1 foot.
2.5 centimeters = about 1 inch.

The customary abbreviations of the linear denominations are meter, m.; decimeter, dm.; centimeter, cm.; and millimeter, mm.

The unit of weight is the **gram**. It is a small weight, being only about one thirtieth of an ounce. A five-cent coin weighs approximately five grams. The weights of small objects and the small quantities used in chemical analysis are expressed in terms of the gram. The weights of heavy objects and large quantities are often expressed in terms of the kilogram, which is 1000 times heavier than the gram. Just as the meter is subdivided, so the gram is subdivided decimally into smaller weights called the decigram, centigram, and milligram. Therefore, a gram contains 10 decigrams, 100 centigrams, or 1000 milligrams; and a kilogram contains 1000 grams.

The gram, decigram, centigram, milligram, and occasionally the kilogram, are used in physical science, though the gram is the most common denomination. For example, if an object weighs 2 grams, 2 centigrams, and 5 milligrams, the weight is expressed as 2.025 grams; similarly, 5 milligrams is often expressed as .005 gram. Preferable abbreviations of the weight denominations are gram, gm.; decigram, dg.; centigram, cg.; milligram, mg.; and kilogram, kg.

The unit of volume is the **liter**. It is slightly larger than a quart, and is used for both dry and liquid measure. As in the case of the meter and the gram, the liter is subdivided into denominations called the deciliter, etc. But these fractional denominations are seldom used. That is, small volumes are not expressed as decimal fractions of a liter, but as cubic centimeters. A liter contains 1000 cubic centimeters, and parts of a liter are designated by the proper number of cubic centimeters. For example, one half a liter is called 500 cubic centimeters, one fourth is 250 cubic centimeters, one tenth is 100 cubic centimeters; two liters is often called 2000 cubic centimeters. The relation of cubic centimeters to a liter is simple. The French chemists who devised the metric system first found the length of the meter by measuring a part of the meridian passing near Paris. Subsequently, they constructed a vessel equal to the capacity of a cubical vessel having edges 10 centimeters long; such a cubical vessel contains, of course, 1000 cubic centimeters. The capacity of this vessel they named the liter. Therefore, the liter and 1000 cubic centimeters are identical, whatever the substance measured — a fact to remember. The abbreviation of liter is l., and of cubic centimeter is cc. or $cm.^3$.

The relation between meter and liter has been shown. Another important relation should be noted. The cubical vessel named the liter may, of course, be filled with any substance; if it is filled with pure water at 4° C., that weight of water is called a kilogram. Therefore in the case of water the following relation exists: 1 liter, 1 quart, and 1000 cubic centimeters weigh approximately the same as 1 kilogram, 1000 grams, and 2.2 pounds. Since many liquids have about the same specific gravity as water, this general relation is useful, and should be learned. It is clear from the relation just given that 1 cubic centimeter of water weighs 1 gram — a fact to remember, since this relation enables us to convert volume into weight, and *vice versa*.

The relation between the units, multiples, and submultiples of the metric system is shown in the —

TABLE OF THE METRIC SYSTEM

| LENGTH | WEIGHT | VOLUME | NOTATION |
|---|---|---|---|
| Kilometer | Kilogram | Kiloliter | 1000. |
| Hectometer | Hectogram | Hectoliter | 100. |
| Decameter | Decagram | Decaliter | 10. |
| METER | GRAM | LITER | 1. |
| Decimeter | Decigram | Deciliter | 0.1 |
| Centimeter | Centigram | Centiliter | 0.01 |
| Millimeter | Milligram | Milliliter | 0.001 |

From this table it is evident that 10 milligrams equal 1 centigram, 10 centigrams equal 1 decigram, 10 decigrams equal 1 gram, and so on.

The relation of the metric system to weights and measures in common use is shown by the —

TABLE OF METRIC EQUIVALENTS

| | | | |
|---|---|---|---|
| 1 meter | = 39.37 inches | 1 inch | = 2.54 centimeters |
| 1 kilometer | = 0.62 mile | 1 mile | = 1.6 kilometers |
| 1 centimeter | = 0.39 inch | 1 cubic inch | = 16.39 cubic centimeters |
| 1 liter | = 0.908 quart (dry) | 1 quart (liq.) | = 0.9465 liter |
| 1 liter | = 1.056 quarts (liq.) | 1 pound (avoir.) | = 0.4536 kilogram |
| 1 gram | = 15.452 grains | 1 ounce (avoir.) | = 28.35 grams |
| 1 kilogram | = 2.2 pounds (avoir.) | 1 ounce (troy) | = 31.1 grams |
| 1 metric ton | = 2204 pounds | 1 grain (apoth.) | = 0.0648 gram |

The passage from the English to the metric system may be accomplished by utilizing the —

TABLE OF METRIC TRANSFORMATION

| TO CHANGE | MULTIPLY BY |
|---|---|
| Inches to centimeters | 2.54 |
| Centimeters to inches | 0.3937 |
| Cubic inches to cubic centimeters | 16.387 |
| Cubic centimeters to cubic inches | 0.061 |
| Ounces to grams (avoir.) | 28.35 |
| Grams to ounces (avoir.) | 0.0353 |
| Grains to grams | 0.0648 |
| Grams to grains | 15.43 |

### Problems

1. What is the abbreviation of gram, centigram, liter, meter, cubic centimeter, centimeter, decimeter, milligram?

2. Express (*a*) 1 liter in cubic centimeters, (*b*) 2 l. in cc., (*c*) 1 meter in centimeters, (*d*) 250 cm. in dm., (*e*) 1 kg. in grams, (*f*) 250 gm. in mg.

3. Add 2 kg., 5 dg., 2 cg., 4 gm., and 7 mg., and express the sum in grams.

4. How many cc. in a liter?

5. What is the weight in grams of (*a*) 1 liter of water, (*b*) 250 cc., (*c*) 500 cc., (*d*) 721 cc.?

6. Express in grams (*a*) 721 kg., (*b*) 62 mg., (*c*) 245 cg., (*d*) 84 dg.

7. Express (*a*) 40 meters in inches, (*b*) 25 kilograms in pounds, (*c*) 54 grams in ounces, (*d*) 72 grams in grains, (*e*) 75 liters in quarts (liq.).

2. **The Thermometer** in scientific use is the **centigrade**. The boiling point of water on this thermometer is 100, and the freezing point is 0 (Fig. 83). The equal spaces between these points are called degrees. The abbreviation for centigrade is C., and for degrees is °. Thus, the boiling point of water is 100° C. Degrees below zero are always designated as minus, *e.g.* − 12° C. means 12 degrees below zero.

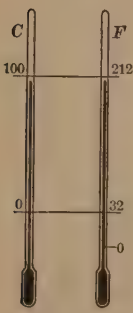


Fig. 83. — Thermometers.

The thermometer in popular use is the **Fahrenheit**. On this instrument the boiling point of water is 212° and the freezing point is 32° above zero (Fig. 83). The abbreviation for Fahrenheit is F.

To change Fahrenheit degrees into the equivalent centigrade degrees, subtract 32 and multiply the remainder by $\frac{5}{9}$, or briefly —

$$C. = \tfrac{5}{9}(F. - 32).$$

To change centigrade degrees into the equivalent Fahrenheit temperature, multiply by $\frac{9}{5}$ and add 32 to the product, or briefly —

$$F. = \tfrac{9}{5}C. + 32.$$

The point −273° C. is called **absolute zero**. Absolute temperature is reckoned from this point. Degrees on the absolute scale are found by adding 273 to the readings on the centigrade thermometer. Thus, 273° absolute is 0° C., 274° absolute is + 1° C., etc.

### Problems

1. Change into Fahrenheit readings the following centigrade readings: (*a*) 60.5, (*b*) 40, (*c*) 92, (*d*) −5, (*e*) 0, (*f*) 100, (*g*) 860, (*h*) −40.

2. Change into centigrade readings the following Fahrenheit readings: (*a*) 207, (*b*) 180, (*c*) 0, (*d*) −30, (*e*) 212, (*f*) 100, (*g*) −40, (*h*) 270.

3. Express the following centigrade readings in absolute readings: (*a*) 0, (*b*) 24, (*c*) −13, (*d*) −260.

3. **Crystallization.** — Most substances in passing from a liquid or a gas into a solid assume a definite shape. This change is called crystallization, and the substances are said to crystallize or to form crystals. Crystals are produced by (1) evaporating a solution, (2) cooling a melted solid, or (3) cooling a vapor. Thus, sodium chloride crystals are formed by evaporating a salt solution; sulphur crystals, by melting and then cooling sulphur; and iodine crystals, by heating iodine in a test tube. These methods are called, respectively, evaporation, fusion, and sublimation.

As a rule, each substance has an individual crystal form by which it can be distinguished. Although there are thousands of different crystals, all belong to one of six classes or systems. This classification is based upon two assumptions: (1) all crystals contain certain lines called axes, and (2) the surfaces or faces are grouped around the axes in definite positions. The axes connect angles, edges, or faces, which are similarly situated on opposite sides of the crystal. The bounding planes or faces are arranged symmetrically around the axes, which also determine (by their lengths and relative positions) the positions of the bounding planes. For example, the cube has three equal axes at right angles to one another and terminating in the center of each of the six bounding surfaces.

The following is a brief description of the six systems of crystallization: —

Fig. 84. — Isometric crystals (cube, octahedron, dodecahedron).

(1) **Isometric.** — This has three equal axes intersecting at right angles. The simplest forms are the cube, octahedron, and dodeca-

hedron (Fig. 84). Substances crystallizing in this system are diamond, common salt, alum, fluor spar, iron pyrites, and garnet.

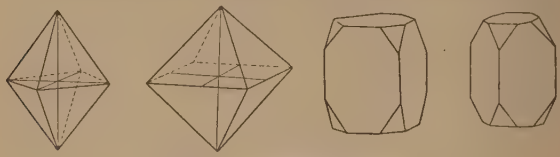


FIG. 85. — Tetragonal crystals.

(2) **Tetragonal.** — This has three axes at right angles; but one axis is shorter or longer than the other two, which are equal. The common forms are the prism, pyramid, and their combinations (Fig. 85). Tin dioxide and zircon form tetragonal crystals.

FIG. 86. — Orthorhombic crystals.

(3) **Orthorhombic.** — This has three unequal axes intersecting at right angles. Common forms are the prism, pyramid, and their combinations (Fig. 86). Potassium nitrate, barium sulphate, topaz, and native sulphur crystallize in this system.

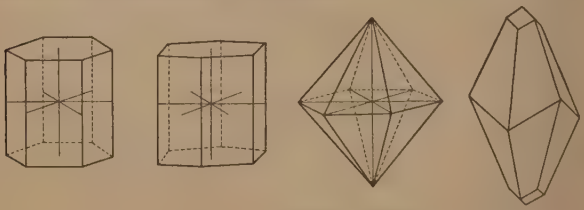


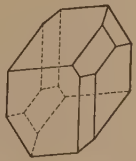
FIG. 87. — Hexagonal crystals.

(4) **Hexagonal.** — This has four axes: three are equal and intersect at 60° in the same plane; the fourth is longer or shorter than the others and is at right angles to their plane. It is a complex

system. Common forms are the prism, pyramid, rhombohedron, scalenohedron, and their combinations (Fig. 87). In this extensive system are found quartz, calcite, beryl, corundum, and ice (see Figs. 60 and 71).

(5) **Monoclinic.** — This has three unequal axes: two cut each other obliquely, and the third is at right angles to the plane of the other two. Common forms are combinations of prisms. It is a complex system, but includes many substances, *e.g.* sulphur deposited by fusion, sodium carbonate, borax, gypsum, and ferrous sulphate (Fig. 88).

FIG. 88. — Monoclinic crystal.



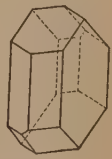


FIG. 89. — Triclinic crystals.

(6) **Triclinic.** — This has three unequal axes, all intersecting at oblique angles. Common forms are complex combinations. Copper sulphate, potassium dichromate, boric acid, and several minerals form triclinic crystals (Fig. 89).

4. **Vapor Pressure.** — The value of **a** in the formula in Chapter V can be found in the

TABLE OF VAPOR PRESSURE

| *a* | mm. | *a* | mm. | *a* | mm. | *a* | mm. |
|---|---|---|---|---|---|---|---|
| 10 | 9.17 | 16 | 13.54 | 22 | 19.66 | 28 | 28.10 |
| .5 | 9.47 | .5 | 13.97 | .5 | 20.27 | .5 | 28.93 |
| 11 | 9.79 | 17 | 14.42 | 23 | 20.89 | 29 | 29.78 |
| .5 | 10.12 | .5 | 14.88 | .5 | 21.53 | .5 | 30.65 |
| 12 | 10.46 | 18 | 15.36 | 24 | 22.18 | 30 | 31.55 |
| .5 | 10.80 | .5 | 15.85 | .5 | 22.86 | .5 | 32.46 |
| 13 | 11.16 | 19 | 16.35 | 25 | 23.55 | 31 | 33.41 |
| .5 | 11.53 | .5 | 16.86 | .5 | 24.26 | .5 | 34.37 |
| 14 | 11.91 | 20 | 17.39 | 26 | 24.99 | 32 | 35.36 |
| .5 | 12.30 | .5 | 17.94 | .5 | 25.74 | .5 | 36.37 |
| 15 | 12.70 | 21 | 18.50 | 27 | 26.51 | 33 | 37.41 |
| .5 | 13.11 | .5 | 19.07 | .5 | 27.29 | .5 | 38.47 |

5. **Atomic Weights.** — The following is a table of

INTERNATIONAL ATOMIC WEIGHTS (1909)

| ELEMENT | SYMBOL | AT. WT. | ELEMENT | SYMBOL | AT. WT. |
|---|---|---|---|---|---|
| Aluminium | Al | 27.1 | Molybdenum | Mo | 96.0 |
| Antimony | Sb | 120.2 | Neodymium | Nd | 144.3 |
| Argon | A | 39.9 | Neon | Ne | 20.0 |
| Arsenic | As | 75.0 | Nickel | Ni | 58.68 |
| Barium | Ba | 137.37 | Nitrogen | N | 14.01 |
| Bismuth | Bi | 208.0 | Osmium | Os | 190.9 |
| Boron | B | 11.0 | Oxygen | O | 16.00 |
| Bromine | Br | 79.92 | Palladium | Pd | 106.7 |
| Cadmium | Cd | 112.40 | Phosphorus | P | 31.0 |
| Caesium | Cs | 132.81 | Platinum | Pt | 195.0 |
| Calcium | Ca | 40.09 | Potassium | K | 39.10 |
| Carbon | C | 12.00 | Praseodymium | Pr | 140.6 |
| Cerium | Ce | 140.25 | Radium | Ra | 226.4 |
| Chlorine | Cl | 35.46 | Rhodium | Rh | 102.9 |
| Chromium | Cr | 52.1 | Rubidium | Rb | 85.45 |
| Cobalt | Co | 58.97 | Ruthenium | Ru | 101.7 |
| Columbium | Cb | 93.5 | Samarium | Sa | 150.4 |
| Copper | Cu | 63.57 | Scandium | Sc | 44.1 |
| Dysprosium | Dy | 162.5 | Selenium | Se | 79.2 |
| Erbium | Er | 167.4 | Silicon | Si | 28.3 |
| Europium | Eu | 152.0 | Silver | Ag | 107.88 |
| Fluorine | F | 19.0 | Sodium | Na | 23.00 |
| Gadolinium | Gd | 157.3 | Strontium | Sr | 87.62 |
| Gallium | Ga | 69.9 | Sulphur | S | 32.07 |
| Germanium | Ge | 72.5 | Tantalum | Ta | 181.0 |
| Glucinum | Gl | 9.1 | Tellurium | Te | 127.5 |
| Gold | Au | 197.2 | Terbium | Tb | 159.2 |
| Helium | He | 4.0 | Thallium | Tl | 204.0 |
| Hydrogen | H | 1.008 | Thorium | Th | 232.42 |
| Indium | In | 114.8 | Thulium | Tm | 168.5 |
| Iodine | I | 126.92 | Tin | Sn | 119.0 |
| Iridium | Ir | 193.1 | Titanium | Ti | 48.1 |
| Iron | Fe | 55.85 | Tungsten | W | 184.0 |
| Krypton | Kr | 81.8 | Uranium | U | 238.5 |
| Lanthanum | La | 139.0 | Vanadium | V | 51.2 |
| Lead | Pb | 207.10 | Xenon | Xe | 128.0 |
| Lithium | Li | 7.00 | Ytterbium (Neoytterbium) | Yb | 172.0 |
| Lutecium | Lu | 174.0 | Yttrium | Y | 89.0 |
| Magnesium | Mg | 24.32 | Zinc | Zn | 65.37 |
| Manganese | Mn | 54.93 | Zirconium | Zr | 90.6 |
| Mercury | Hg | 200.0 | | | |

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Outline for study of Metals.

Luster
Color
Sp. gr.
Hardness
Ductility
Malleability
Opaqueness
Conductivity.

1
Chromium
Cobalt
Nickel.

2
Manganese
Zinc
Magnesium

3
Calcium
Barium
Strontium

4 Iodium.

5 Potassium
ammonium

## International and Approximate Atomic Weights

| Element | Symbol | Inter. | Approx. At. Wt. |
|---|---|---|---|
| Aluminium | Al | 27.1 | 27 |
| Antimony | Sb | 120.2 | 120 |
| Arsenic | As | 75.0 | 75 |
| Barium | Ba | 137.37 | 137 |
| Bismuth | Bi | 208.0 | 208 |
| Boron | B | 11.0 | 11 |
| Bromine | Br | 79.92 | 80 |
| Cadmium | Cd | 112.40 | 112 |
| Calcium | Ca | 40.09 | 40 |
| Carbon | C | 12.00 | 12 |
| Chlorine | Cl | 35.46 | 35.5 |
| Chromium | Cr | 52.1 | 52 |
| Cobalt | Co | 58.97 | 59 |
| Copper | Cu | 63.57 | 63.5 |
| Fluorine | F | 19.0 | 19 |
| Gold | Au | 197.2 | 197 |
| Hydrogen | H | 1.008 | 1 |
| Iodine | I | 126.92 | 127 |
| Iron | Fe | 55.85 | 56 |
| Lead | Pb | 207.10 | 207 |
| Lithium | Li | 7.00 | 7 |
| Magnesium | Mg | 24.32 | 24 |
| Manganese | Mn | 54.93 | 55 |
| Mercury | Hg | 200.0 | 200 |
| Nickel | Ni | 58.68 | 58.5 |
| Nitrogen | N | 14.01 | 14 |
| Oxygen | O | 16.00 | 16 |
| Phosphorus | P | 31.0 | 31 |
| Platinum | Pt | 195.0 | 195 |
| Potassium | K | 39.10 | 39 |
| Radium | Ra | 226.4 | 226.5 |
| Silicon | Si | 28.3 | 28 |
| Silver | Ag | 107.88 | 108 |
| Sodium | Na | 23.00 | 23 |
| Strontium | Sr | 87.62 | 87.5 |
| Sulphur | S | 32.07 | 32 |
| Tin | Sn | 119.0 | 119 |
| Zinc | Zn | 65.37 | 65 |

The international atomic weights, given above, are taken from the 1909 table. The approximate atomic weights are supplied by the author and are designed to facilitate the solution of problems.

S0-CRU-875